PART 1

1992 MICHTOX: A MASS BALANCE AND BIOACCUMULATION MODEL FOR TOXIC CHEMICALS IN LAKE MICHIGAN

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1.1 Executive Summary

A mass balance model has been developed for critical pollutants (except mercury) in Lake Michigan. The model predicts chemical concentrations in 17 water and sediment segments in response to atmospheric and tributary loadings. It was designed to predict chemical concentrations in the open waters of Lake Michigan, with additional nearshore resolution in Green Bay. The model was calibrated using existing information to define water circulation and the particle balance.

A bioaccumulation model has also been developed for critical pollutants in Lake Michigan. The model predicts chemical accumulation in lake trout and bloater by pelagic and benthic food chains. The bioaccumulation model is coupled to the mass balance model for exposure to chemicals in water and sediment in southern Lake Michigan. By this coupling, chemical accumulation in biota is predicted in response to loadings.

The model is capable of either dynamic (time variable) or steady-state simulations. A simplified steady-state model was developed for performing sensitivity and uncertainty analysis. Chemical-specific partitioning, fate, and bioaccumulation processes were parameterized solely by physicochemical properties including octanol-water partition coefficient, vapor pressure, Henry's constant, photolysis rate, and rate of metabolism in fish. Atmospheric input of a chemical was based upon the ambient air concentration of each chemical.

Model predictions were validated using data for plutonium, lead, and polychlorinated biphenyls (PCBs). Because MICHTOX was not calibrated using toxic chemical data for Lake Michigan, validation represents an independent test of the model predictions as well as the assumptions, simplifications, and aggregations that were used to build the model. Plutonium data validated the particle transport calibration. Seasonal stratification was demonstrated to be an important process determining long-term chemical dynamics. Toxic chemical fate, transport, and bioaccumulation were validated using PCBs data. A time-series of PCBs loading to Lake Michigan was developed based upon a review of estimates made by other researchers. The model was run for the period 1940-1990 using these loadings, and the resulting predictions were compared to available data. Predictions of PCBs water concentrations in southern Lake Michigan were in good agreement with limited data. Southern Lake Michigan sediment concentration and water and sediment concentration predictions in Green Bay also

agreed qualitatively with available data. Predictions of lake trout PCBs concentrations did not exactly match details of the concentration trends in the data. However, the prediction was acceptable considering the accuracy of the PCBs loadings and possible data quality concerns. Predicted PCBs concentrations in bloater were also in agreement with available data, further validating the bioaccumulation predictions. The results of model validation using PCBs were generally better than expected considering the preliminary nature of this model.

The steady-state model solution was used to generate load-response predictions and mass fate and transport fluxes, to examine model sensitivity, and to estimate predictive uncertainty. The mass balance for toxic chemicals was dominated by internal fluxes associated with particles (settling and resuspension) and particle burial, volatilization, and photolysis. The relative magnitude of these fluxes, and hence, the model sensitivity to parameterization, were found to vary between chemicals and model segments. Transport of the critical pollutants between lake basins or from Green Bay to the main lake was not significant. Volatilization and redeposition is likely to be a much more significant transport mechanism.

At steady-state, a linear relationship between total loading and concentrations was predicted. Monte Carlo analysis was used to estimate the uncertainty in model predictions. In terms of the width of the 95% confidence interval, predictive uncertainty was on the order of 10 times for concentrations in water, and 30-300 times for concentrations in trout. The confidence intervals "bracket" the load-concentration predictions and define the expected bounds of model error due to parameterization. The magnitude of predictive uncertainty suggests that model results may be qualitatively useful, for instance, in comparing alternative simulations, but quantitative use of the results would be inappropriate. Uncertainty analysis was also used to identify "critically" uncertain model parameters to be prioritized for process research.

Several factors complicate the relationship between loads and concentrations. First, reducing the load from only one source category (tributaries, for instance) will have a less-than-proportional effect upon concentrations. PCBs concentrations, for example, were demonstrated to be largely insensitive to reduced tributary loads. Another factor was the "lag time" in concentration response to loading reduction. For the critical pollutants in Lake Michigan, lag time reflects the large inventory of chemicals in the sediments. The effectiveness of loading reduction (even reductions to zero load) at a given time is ultimately constrained by the system lag time. Dynamic model predictions were used to predict the long-term rate of concentration decline following loading reduction for each toxic chemical.

The model was used to predict the effect of eliminating tributary and total PCBs loadings, compared to a "No-Action" scenario of constant PCBs loading after 1990. The results suggest that significant reductions in trout PCBs concentrations will occur in the next 10 years, even if no additional loading reductions are made. Additional reductions of PCBs concentrations in Lake Michigan will be achieved only if significant reductions in atmospheric sources are made. These results are, however, uncertain because the PCBs loading history is poorly defined and because of potential errors in the parameterization of the surficial sediment layer thickness.

The model was also used to predict the potential impact of a severe storm "event" on the remobilization of toxic chemical from the lake sediments. A two-day storm resuspending the entire surficial sediment layer in southern Lake Michigan resulted in elevated total water column PCBs for almost a year. However, because most of the resuspended PCBs remain sorbed to particles, the effect of the storm upon biota concentrations was negligible.

Finally, uncertainty in the dynamic model predictions was evaluated. The thickness of the surficial sediment layer, which determines the residence time of particles and particle-associated contaminants in the lake, was demonstrated to be a critical parameter. Uncertainty in initial concentrations, loading history, and dynamics of the Lake Michigan trophic structure were considered as additional factors leading to uncertainty in model predictions.

1.2 Recommendations

1.2.1 Verification of Model Predictions

A high priority should be placed upon generating data of known quality and consistency for the purpose of model verification. Further verification to contemporary data is necessary to quantitatively demonstrate the predictive ability of the model. Such a demonstration is the fundamental test of a model's adequacy as a predictive tool. Data should be collected for all chemicals that are identified as the highest priority toxics. (For critical pollutant "mixtures," chemical-specific representatives of the mixture should be quantified.) These data would include representative measurements of the following:

1.2.1.1 Air Concentrations/Deposition Fluxes

Air concentrations and deposition fluxes should be measured, on at least a seasonal basis, over each lake basin with additional measurements near likely emission sources (urban/industrial areas). If based upon shore station measurements, then methods for over-lake extrapolation must be devised.

1.2.1.2 Surficial Sediment Concentrations

The distribution of chemical concentrations and organic carbon in surficial sediment should be characterized similar to the 1975 sediment survey (Frank *et al*., 1979). This should be accompanied by more limited sediment core sampling in focusing zones to measure vertical distributions of contaminants and particle tracers. Near-surface distribution should be resolved on 1 cm or finer intervals.

1.2.1.3 Lake Trout

Lake trout should be sampled from different lake regions, including the nearshore and reef zones. Chemical concentrations and lipid should be measured in age seven male and female trout. It would be preferable to analyze individual fish instead of composites. Analysis of whole fish would be preferred.

1.2.1.4 Major Tributaries

Chemical loads should be determined for all major tributaries to Lake Michigan. Monitoring should be conducted at a location on each tributary where lake water inflow does not persist except during low flow. Point sources below the monitoring location should be sampled separately. Total chemical concentration, particulate and dissolved organic carbon, total suspended solids, chlorophyll, and chloride should be measured based upon flow-proportioned sampling. Flow, conductivity, transmissivity, and temperature should be measured daily (or hourly, for event responsive tributaries). Chemical monitoring should be proceeded or at least accompanied by evaluation of in-place sediment contamination. In-place pollutants may be mobilized only under extremely high flows; their contribution to tributary loading is, therefore, unlikely to be detected by conventional monitoring.

1.2.1.5 Water

Chemical concentrations (dissolved and particulate) should be measured in the main lake basins. Particulate and dissolved organic carbon, total suspended solids, chlorophyll, and other standard limnological parameters should also be measured. Sampling should be conducted during both stratified and unstratified periods, with mid-epilimnion, metalimnion, mid-hypolimnion, and benthic nephloid sampling during stratification. A true field blank for dissolved and particulate chemicals must also be obtained to validate these measurements.

Although the effort and cost associated with such an undertaking would be substantial, it may be argued that most of these data would be necessary to justify additional priority toxics load reductions regardless of modeling effort.

1.2.2 Extend Model to Other Critical Pollutants and Target Organisms

It may be necessary to extend the modeling effort to other critical pollutants. Mercury is one such chemical that is not addressed by the present model. Existing mercury models, most notably the Electric Power Research Institute (EPRI) Mercury Cycling Model (Hudson *et al*., 1991) lack the flexibility to simulate site-specific conditions for the Great Lakes. A substantial process research effort will be necessary before management-level simulation of mercury mass balance, transformation, and bioaccumulation can be made. Planning for such efforts by organizations such as the Mid-Continent Ecology Division (MED)-Duluth are underway; rapid progress is not expected, given the many fundamental unknowns regarding mercury's behavior in the ecosystem. Extensive monitoring of loads and ambient concentrations in Lake Michigan will be necessary as well, as virtually no mercury data exist for this system. This will require the development of analytical capabilities that presently do not exist. Thus, the process of developing models for other critical pollutants may be lengthy.

It may also be necessary to extend the modeling effort to other target organisms. These could include a variety of birds and wildlife which consume fish from the lake: mink, otter, heron, cormorants, eagles, gulls, terns, and turtles. Although toxicokinetics of hydrophobic organic chemicals (HOCs) in herring gulls have been studied (Clark *et al*., 1987), top predators other than fish have not been incorporated in bioaccumulation models. This would, again, necessitate a developmental effort.

1.2.3 Further Model Development

Further development of mass balance and bioaccumulation models for priority toxics in Lake Michigan may be justified for at least two reasons: to improve the scientific credibility of the model and to improve the accuracy and resolution of model predictions. Because the development of the model was based largely upon existing information, numerous aspects of the structure and parameterization of MICHTOX lack adequate justification to establish scientific credibility. Furthermore, a variety of assumptions which are critical to model performance have not been validated. To go beyond a management-level application, which has limited acceptance and/or utility, will require the resolution of these issues. In part, this resolution may be achieved by obtaining the proper calibration/verification data for toxic chemicals in Lake Michigan. However, specific process research to improve process descriptions and parameterization will also be necessary. These processes include:

- Chemical properties: octanol-water partition coefficient, Henry's constant, photolysis rate
- Particle transport at the water-sediment interface
- Chemical partitioning to organic carbon and plankton
- Atmospheric deposition fluxes
- Chemical metabolism
- Chemical assimilation efficiency, particularly in benthos

The second aspect of further model development is improving the predictive ability of the model. Predictive ability, in terms of both accuracy and resolution of predictions, may be improved by incorporating more fundamental and realistic process descriptions and linkages in the simulation. This, in turn, will allow for finer spatial and temporal resolution of predictions. Specific areas for further development include the following:

1.2.3.1 Circulation

In the WASP models, circulation is specified as advective and dispersive transport functions. This approach has the disadvantages that calibration of the transport function requires extensive tracer data, circulation is not predicted by meteorologic forcing functions, and (practically) the model loses resolution because of the difficulty in measuring/calibrating fine-scale transport variability. The alternative approach is to predict circulation using hydrodynamic models, which are based upon momentum and continuity balances in two or preferably, three dimensions. Hydrodynamic predictions are driven by meteorologic forcing functions and provide fine-scale spatial and temporal resolution. Basing circulation simulations on hydrodynamics will be necessary for accurate mass balance modeling in nearshore zones.

1.2.3.2 Sediment Transport

Particle transport is specified as velocity fields in the WASP models, and is based upon calibration. This approach is descriptive rather than predictive. It does not relate particle transport to actual forcing functions, and its accuracy and resolution are limited by measurement availability. Sediment transport models, which predict the settling and resuspension of particles as functions of shear stress, aggregation/disaggregation, and compaction in the sediment bed, could be coupled to the mass balance to overcome these limitations. As was the case for hydrodynamics, this coupling would be particularly important in shallow, nearshore zones where sediment resuspension is highly episodic. Sediment transport coupling would also be very useful in predicting particle redistribution and focusing, which produce complex contaminant distributions in Lake Michigan sediments.

1.2.3.3 Organic Carbon Dynamics

Present toxic chemical mass balance models treat suspended particles as fundamentally abiotic. Yet most of the particulate matter in the Great Lakes water column is phytoplankton, at least during the growing season. Organic carbon, the principal sorbent for HOCs, is therefore, cycled largely by biotic processes – production, grazing, respiration, and decay. Because phytoplankton and toxic chemicals are states related through organic carbon, their behavior is expected to be coupled. Building a model with this coupling is a principal research objective of the Green Bay Mass Balance Project (GBMBP). Not only would this coupling improve model realism and accuracy, but it would also allow the model to simulate how nutrient control may impact toxic chemicals in the ecosystem.

1.2.3.4 Food Chain Variability and Dynamics

The WASTOX food chain model, which was adapted for use in MICHTOX, predicts bioaccumulation for "representative" (i.e., average) organisms. This population-based model has been validated in a number of ecosystem/contaminant applications. Yet it is unclear whether this model is capable of describing the variability in bioaccumulation observed for organisms in many data sets. Individual-based bioaccumulation models have been proposed (Hallam *et al*., 1990) as an alternative to the population-based model, offering the advantage of treating bioenergetic parameters and exposure histories as functions of the individual organism. Bioaccumulation predicted for many individuals then defines the probability distribution for the population or species, which in some instances (i.e., risk assessment) may be important to predict. This approach to modeling may be particularly advantageous at the point of modeling effects of bioaccumulating chemicals, where a given body burden may affect only a portion of the population.

Another weakness of the present bioaccumulation model is the static structure of the food chain. This limitation is discussed in Section 1.7.4. Just as toxic chemical dynamics are coupled to those of phytoplankton, there may be linkages to higher trophic levels as well. In particular, as the structure of the food chain changes, so may bioaccumulation in higher trophic levels. Ecosystem models capable of simulating the dynamics of trophic structure have been developed and proposed (DePinto,1990). Their data requirements are extensive, however, and their predictive ability in systems as large as the Great Lakes is unknown. The linkage of bioaccumulation and ecosystem models is probably the most ambitious modeling recommendation, but it would provide the ability to predict the consequences of stresses such as fisheries management and exotic species in terms of population diversity and bioaccumulation.

1.2.4 Establish Linkages to Atmospheric and Watershed Models

A final aspect of model development that would be particularly useful for management, as well as scientific applications, is the linkage of the water quality model to mass balance simulations in the atmosphere and watershed. This linkage is necessary to relate actual sources of toxics to their delivery to (and removal from) the lake, instead of measuring this delivery as loads. The linkage to atmospheric mass balance is particularly critical, because it is not at all apparent that present measurements of atmospheric concentrations and deposition fluxes are free of the "boundary effects" due to volatilizing chemicals. Furthermore, the atmospheric transport and subsequent redeposition of volatilizing chemicals can only be simulated by coupling air and water mass balances.

1.3 Introduction

1.3.1 Project Objectives

This report describes the development and application of MICHTOX, a toxic chemical mass balance and bioaccumulation model for Lake Michigan. This work was supported by the United States Environmental Protection Agency (USEPA) Region V, which requested the MED-Duluth/Large Lakes and Rivers Forecasting Research Branch (LLRFRB) to develop a mathematical model for Lake Michigan. The primary objective of modeling was to provide guidance to Region V and the Lake Michigan Lake-wide Management Plan (LaMP) as to expected water quality improvements in response to critical pollutant loading reductions. A secondary objective was to demonstrate the potential utility of the mass balance modeling approach. The model addressed two primary questions related to the LaMP.

1. For chemicals identified as critical pollutants, what is the relationship between loads from the atmosphere, tributaries, point sources, and ground water to concentrations in water, sediment, and biota in Lake Michigan?

2. If the loads of these chemicals to Lake Michigan were reduced, how rapidly would concentrations change?

In response, a management-level model has been developed which, within expected confidence limits, addresses these management questions. The loading-concentration relationship was modeled for 11 critical pollutants:

Benzo(a)pyrene (BaP)
Chlordane (total chlordane and nonachlor isomers)
Total dichlorodiphenyltrichloroethane (DDT)
 [p,p'-DDT, -dichlorodiphenyldichloroethylene (DDE) and -dichlorodiphenyldichloroethane (DDD)]
Dieldrin
Heptachlor epoxide
Hexachlorobenzene (HCB)
Lead
Total PCBs
2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)
2,3,7,8-tetrachlorodibenzofuran (TCDF)
Toxaphene

The scope of this project was ambitious; indeed, no water quality model intended to simulate as many different toxic chemicals in such a large system had been previously developed.

The model is based upon available theory and data characterizing the sources, transport, fate, and bioaccumulation of toxic chemicals in Lake Michigan and the other Great Lakes. It builds upon 15 years of Great Lakes modeling research sponsored and conducted by the USEPA. The results of MICHTOX should be considered preliminary because the model is based upon a variety of assumptions which have not been validated for either Lake Michigan or individual toxic chemicals. In addition, significant compromise was made regarding model calibration. The customary application of mass balance models, such as MICHTOX, includes extensive calibration of model parameters to site-specific load, chemical concentration, and process variable data. Calibration is a step of model development necessary for accurate parameterization and simulation. Because only some of the necessary data for calibration were available for toxic chemicals in Lake Michigan, this step of model development could only be partially accomplished. Consequently, it is necessary to consider the magnitude of uncertainty associated with MICHTOX predictions, particularly if the model is to be useful to the LaMP. Past experience has demonstrated that quantifying predictive uncertainty is essential to credible model application for management purposes. To this end, extensive analysis of model uncertainty was applied to the model. MICHTOX is intended to be a valid representation of current understanding of toxic chemical transport, fate, and bioaccumulation processes in the Lake Michigan ecosystem; however, it also reflects the significant limitations of this knowledge.

Besides addressing the two primary questions above, the process of applying the model reveals further research and data needs. These include identifying shortcomings and potential inconsistencies in the database for toxic chemicals in Lake Michigan as well as limitations of the modeling approach due to poor model resolution, uncertainty in model structure, process formulations, and parameterization. Such identification of research and data needs serves as a useful planning exercise prior to large-scale project(s) designed to improve our understanding of toxic chemical behavior in the ecosystem.

1.3.2 Lake Michigan Toxics Problem

The long-term trend of toxic chemical contamination of Lake Michigan is well illustrated by merging two United States Fish and Wildlife Service (USFWS) data sets for chemical concentrations in small fish (Neidermeyer and Hickey, 1976; Hesselberg *et al*., 1990). The result shows an abrupt rise in PCBs and DDT concentrations beginning around 1950 (Figure 1.1). Concentrations peak somewhere between 1960 and 1970, then decline almost as abruptly. Similar trends throughout the Great Lakes have been correlated to chemical production and usage rates (Oliver *et al*., 1989; Eisenreich *et al*., 1989). However, concentrations during the last 10 years appear to be nearly constant at values elevated above pre-contamination conditions. Dieldrin concentrations, on the other hand, are much lower but have been steadily increasing since first detected in fish collected around 1950. In general, monitoring of toxic chemicals in Lake Michigan in the past decade suggests little trend in concentrations. Prior to this, concentrations of several toxic chemicals, including chlordane, as well as PCBs and DDT, declined dramatically as bans on chemical production were initiated. What has changed is unclear: has the lake attained equilibrium with continuing loads such as atmospheric deposition, or does variability in the data mask continuing slow declines in toxic chemical concentrations? Resolving this issue is important because further reductions in toxic chemical concentrations appear necessary to protect human health and the ecosystem. Yet, further reductions in loading may or may not be necessary to achieve those concentration reductions. The approach to modeling toxics is strongly related to the desired scale and resolution of the analysis. The Lake Michigan LaMP addresses water quality in the open lake waters, defined to include all waters within the

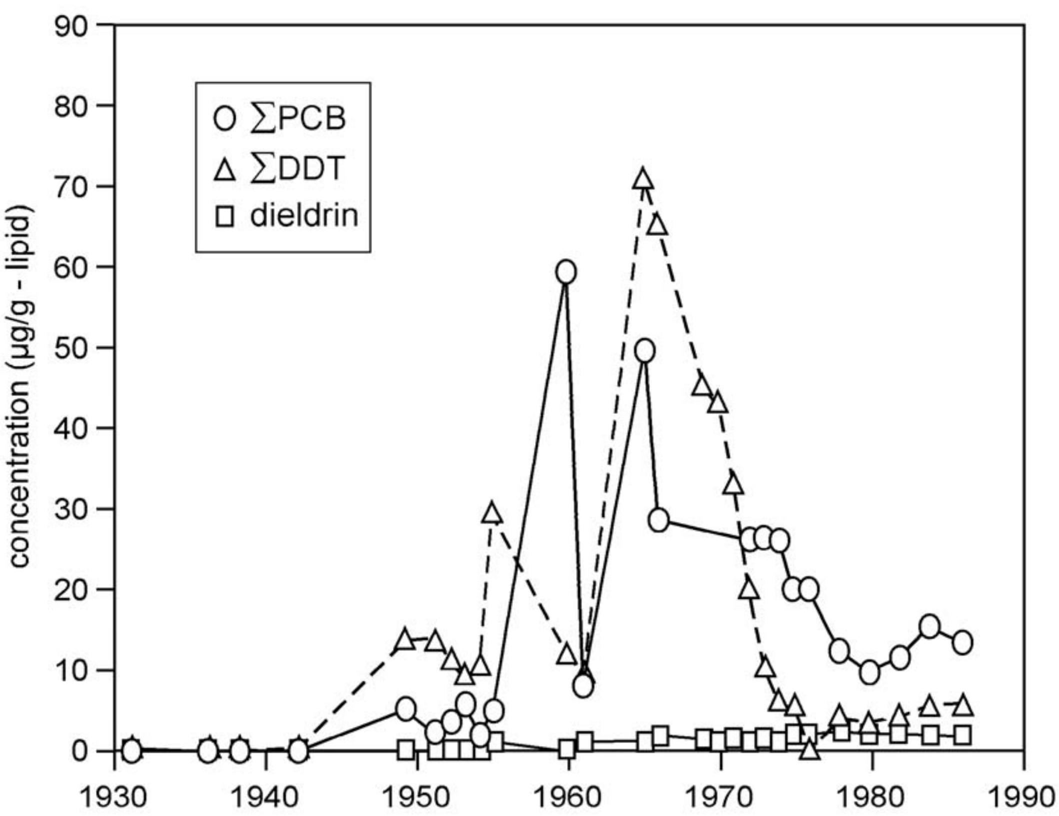


Figure 1.1. Long-term concentration trends for toxic chemicals in small Lake Michigan fish.

lake including all bays, harbors, and inlets. The spatial scale of MICHTOX is on the order of the well-mixed lake basins, with additional model resolution in Green Bay. This specifically excludes the simulation of toxic chemicals in other nearshore regions, because MICHTOX is not predictive at the scale of variability exhibited in the nearshore. Modeling water quality in nearshore regions, such as bays, harbors, and inlets, would require site-specific data collection efforts and potentially different modeling techniques. Of course, this excludes all except one of the 10 Areas of Concern (AOCs) around Lake Michigan. These AOCs should be treated as source components to the mass balance; this remains to be accomplished. As sources, the AOCs may be highly significant. Marti and Armstrong (1990) estimate that half of the tributary loading of PCBs in the early 1980s was discharged from the Fox River. According to Thomann and Kontaxis (1981), the source of 50 to 90% of peak PCBs concentrations in Lake Michigan may have been a single AOC: Waukegan Harbor.

1.4 Model Description

1.4.1 Model Framework

The MICHTOX mass balance model was used to predict chemical concentrations in the water and surficial sediment in response to chemical loads to Lake Michigan. The mass balance model was adapted from the general water quality model WASP4 (Ambrose *et al*., 1988). The model implements mass balance equations describing the input, transport, and fate of hydrophobic toxic chemicals in the Great Lakes. A schematic of the mass balance model for a vertically-segmented lake basin is presented in Figure 1.2. Chemical concentrations in the epilimnion (c_E), hypolimnion (c_H) and surficial sediment (c_S) are calculated by solving the coupled mass balance equations.

The mass balance in the epilimnion is:

$$\frac{d(V_E\ c_E)}{dt}$$

... accumulation of chemical mass

$$= \sum_{I=i}^{n} W_{E,n}$$

chemical loads

$$- E_{EH}\ (c_E - C_H)$$

dispersive exchange with hypolimnion

$$- \Sigma\ E_{EB}\ (c_E - c_B)$$

dispersive exchange with adjacent epilimnion segments

$$- Q_{EB}\ c_E + Q_{BE}\ c_B$$

advective transport to and from adjacent epilimnion segments

$$- v_{S,E}\ A\ f_{sE}\ c_E$$

settling from epilimnion to hypolimnion

$$+ v_{r,H}\ A\ f_{sH}\ c_H$$

resuspension from hypolimnion to epilimnion

$$+ A\,(W_v\ G_r + v_{dry}\ f_{pA}\ c_A)$$

vapor exchange with atmosphere

$$- k_p\ f_{dE}\ V_E\ c_E$$

photolysis

Variables introduced in this equation are defined as follows:

V_s	=	volume of segment S [L^3]
c_S	=	total chemical concentration in segment S [M/L^3]
$W_{S,i}$	=	incremental chemical loading to segment S [M/T]
$E_{S_1 S_2}$	=	bulk dispersive exchange coefficient between segments S_1 and S_2 [L^3/T]

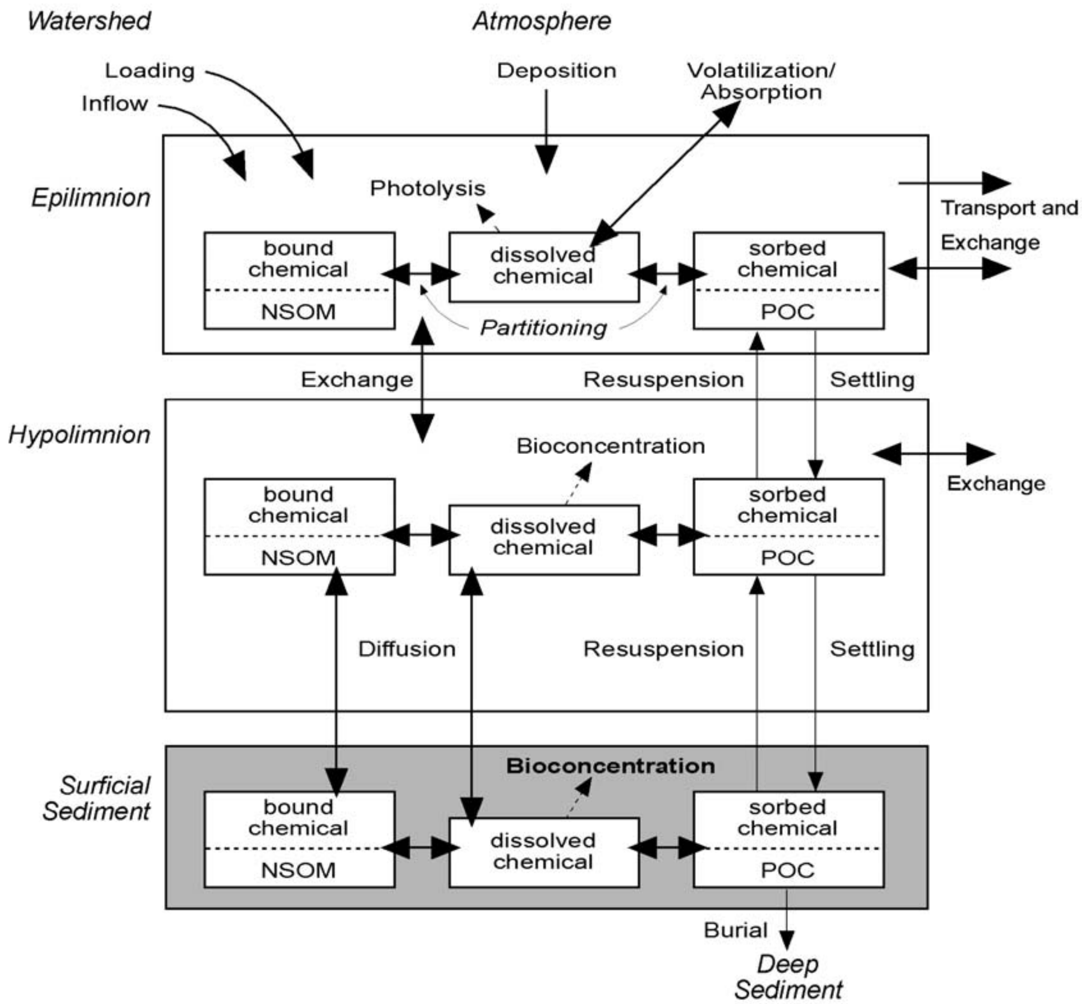


Figure 1.2. MICHTOX mass balance schematic.

$Q_{S_1 S_2}$	=	flow from segments S_1 to S_2 [L^3/T]
f_{dS}, f_{sS}, f_{bS}	=	dissolved, sorbed (to particles), and bound (to non-settling organic matter) chemical fractions in segment S
$v_{s,S}$	=	particle settling velocity from segments S [L/T]
$v_{r,s}$	=	particle resuspension velocity from segment S [L/T]
A	=	surface area [L^2]
c_A	=	total chemical concentration in air [M/L^3]
W_v	=	volumetric washout ratio
G_r	=	rainfall [L/T]
v_{dry}	=	dry deposition velocity [L/T]
f_{vA}, f_{pA}	=	vapor and particulate chemical fractions in air
k_v	=	volatilization rate [L/T]
H’	=	dimensionless Henry’s constant
k_p	=	photolysis rate [L/T]

The mass balance in the hypolimnion is:

$$\frac{d(V_H\, c_H)}{dt}$$

... accumulation of chemical mass

$$- E_{EH}\ (c_E - C_H)$$

dispersive exchange with epilimnion

$$- \Sigma\, E_{HB}\ (c_H - c_B)$$

dispersive exchange with adjacent hypolimnetic segments

$$+ v_{s,E}\ A\ f_{sE}\ c_E$$

settling from epilimnion to hypolimnion

$$- v_{s,H}\ A\ f_{sH}\ c_H$$

settling from hypolimnion to surficial sediment

$$- v_{r,H}\ A\ f_{sH}\ c_H$$

resuspension from hypolimnion to epilimnion

$$+ v_{r,S}\ A\ f_{sS}\ c_S$$

resuspension from surficial sediment to hypolimnion

$$+ K_f A_d\ [f_{dS} + f_{bS}\ \frac{c_S}{n_S} - (f_{dH} + f_{bH})\ c_H]$$

sediment-water diffusion

Additional variables introduced in this equation are:

K_f = diffusive exchange coefficient [L/T]

A_d = sediment deposition area [L^2]

n_s = surficial sediment porosity

The simplification of the mass balance equation for a vertically-integrated (i.e., unstratified) water column has been previously reported (Di Toro, 1987). The mass balance in the surficial sediment is:

$$V_S\, \frac{dc_S}{dt}$$

... accumulation of chemical mass

$$= v_{s,H}\ A\ f_{sH}\ c_H$$

settling from hypolimnion to surficial sediment

$$- v_{r,S}\ A\ f_{sS}\ c_S$$

resuspension from surficial sediment to hypolimnion

$$- K_f\, A_d\ [(f_{dS} + f_{bS})\ \frac{c_S}{n_S} - (f_{dH} + f_{bH})\ c_H]$$

sediment-water diffusion

$$- v_b\ A_d\ f_{sS}\ c_S$$

burial to deeper sediment layers

The only additional variable introduced in the surficial sediment mass balance is v_b, the sediment burial (or sedimentation) velocity [L/T]. A single surficial sediment layer has been used in MICHTOX; this is assumed to be adequate to simulate sediment-water chemical exchange processes. Vertical resolution of chemical concentrations in deeper sediment layers may be obtained from the model by transforming the time scale to sediment depth using the burial (sedimentation) rate.

1.4.2 Segmentation

Lake Michigan is spatially divided into 17 segments in the MICHTOX model, as depicted in Figure 1.3. This segmentation represents an intermediate level of spatial resolution, which balances the desire to predict concentration response to spatially non-uniform loads against a lack of data to either implement or validate a greater level of resolution. The main lake is divided into southern, central, and northern basins, according to the large-scale circulation and sedimentation patterns observed in Lake Michigan. The circulation of the southern and central basins of the lake are characterized by distinct counter-rotating gyres (Schwab, 1983). The shallow northern basin has little depositional sediment and no apparent large-scale circulation, but

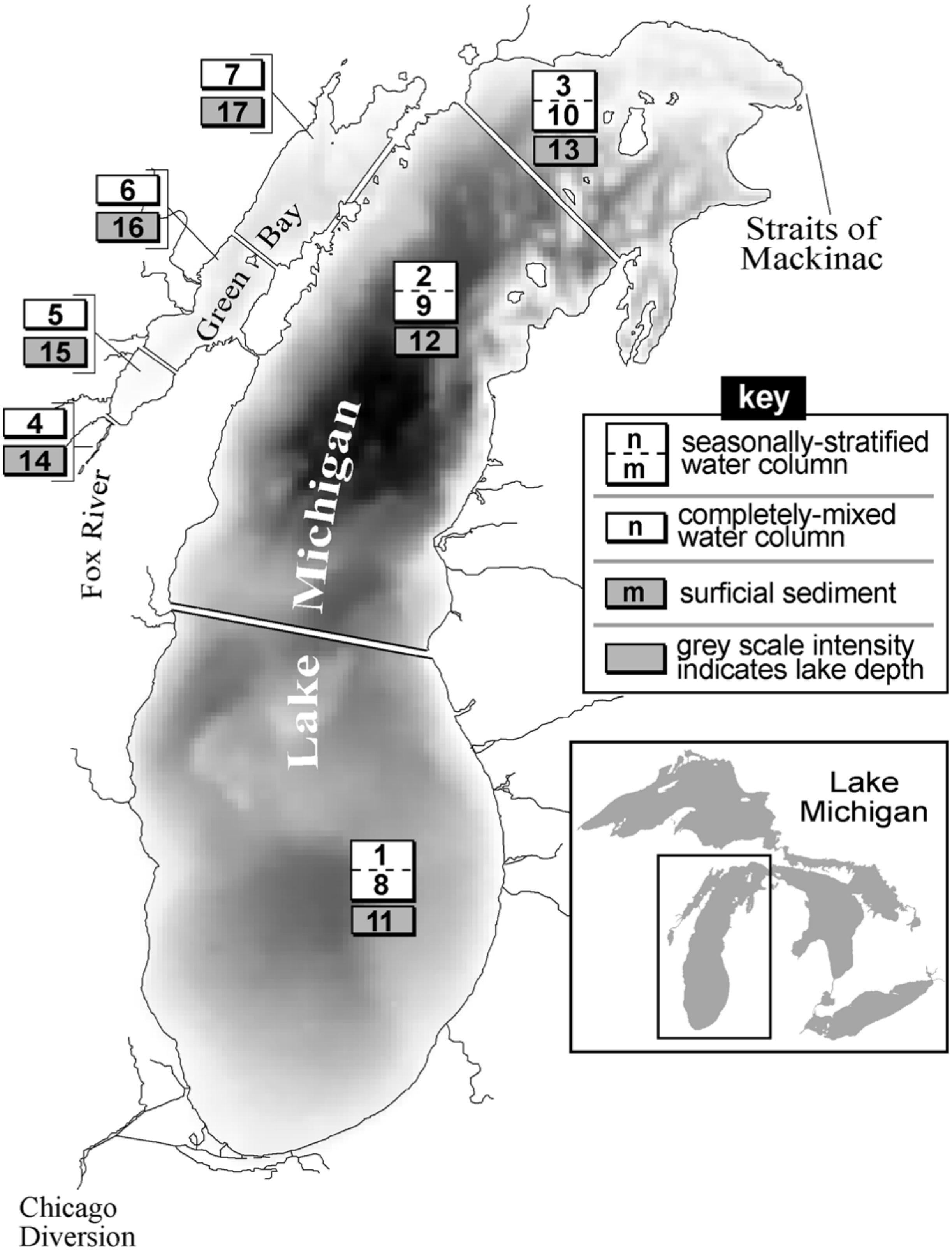


Figure 1.3. Spatial segmentation for the 17 segment MICHTOX model.

undergoes considerable exchange with northern Lake Huron water across the Straits of Mackinac. Each main lake basin is segmented vertically into epilimnion, hypolimnion, and surficial sediment.

Green Bay is divided into three completely-mixed water column and sediment segments. The lower Fox River is represented as a final water/sediment segment pair in the model. Only in these segments does MICHTOX represent nearshore-to-open water gradients. Additional model resolution is provided in Green Bay because (1) significant past and present PCBs loading from the Fox River has resulted in persistent water and sediment concentration gradients, and (2) results here may be compared to those of the calibrated models under development for the GBMBP. In fact, the MICHTOX Green Bay segments are a superset of the segments chosen for the GBMBP model. Segment geometry (volumes, interfacial and surface areas, and depths) were based upon the 2 km digitized bathymetry data of Schwab and Sellers (1980).

1.4.3 Circulation

Lake circulation in MICHTOX is specified as inflows from tributaries, flows and dispersive exchanges between the water column segments, and outflow and exchange across the Straits of Mackinac. Flows were based upon the whole-lake water balance of Quinn (1977), which provided monthly average changes in storage, tributary flow, outflow and diversion, precipitation, and evaporation. Tributary flow was apportioned to the various surface water segments according to the river mouth location and mean flow of the 14 largest Lake Michigan tributaries. Changes in storage, precipitation, and evaporation were apportioned based upon segment surface area. Based upon this water balance, flows between all surface water segments were calculated for each month. Annual hydraulic residence times (volume/outflow) for the main lake segments range from 110 years in the southern basin to seven years in the north. In comparison, the hydraulic residence time for the lake as a whole is 100 years (Winchester, 1969). Hydraulic residence times in Green Bay segments are much shorter: from 0.4 years in the inner bay to four years in the outer bay.

Vertical exchange coefficients, which quantify the extent of mixing between epilimnetic and hypolimnetic segments in the main lake, were taken from the Lake Michigan WASP eutrophication model MICH1 (Rodgers and Salisbury, 1981). These coefficients vary seasonally from minimum values of essentially zero during stratification (from approximately May to October) to maximum values of 15 and 40 cm^2/s (southern and northern lake basins, respectively) during unstratified periods. While vertical exchange was curtailed during the summer, entrainment of hypolimnetic water due to the deepening of the thermocline was simulated. Entrainment "mixes" hypolimnetic water into the epilimnion; however, the mass balance of the hypolimnion is not affected. The thermocline in southern and central lake basins is simulated to deepen from an initial depth of 10 m at the onset of stratification to a maximum depth of 50 m before overturn, based upon data from Robbins and Eadie (1991). In the northern basin, the thermocline was simulated to deepen from 10 to 15 m based upon temperature profile data of Ayers *et al*. (1958).

Horizontal exchange is the mixing of water from adjacent segments due to fluctuations in flow in response to surface shear stress from storms and to rapid surface heating and cooling. Horizontal exchange coefficients in Green Bay were calibrated to reproduce observed chloride gradients. The calibration achieved using 1982 chloride data (Auer, 1989) is shown in Figure 1.4. The horizontal exchange between Green Bay and Lake Michigan was verified by comparison to the bi-directional flows measured in the bay-lake passages in 1977 (Eadie *et al*., 1991) and 1989 (Gottleib *et al*., 1990). The calibrated exchange between bay and lake reaches a maximum during July of 7800 m^3/s, some 30 times greater than the combined tributary inflow to the bay.

Horizontal exchange coefficients were more difficult to define in the main lake, where no similar "tracer" gradients were observed. Values of 100 and 1000 cm^2/s were used in MICH1 for hypolimnetic and epilimnetic horizontal exchange, respectively. These values are similar to the exchange coefficients used by Thomann *et al*. (1979) for Lake Ontario, but they are considerably smaller than the 1000 m^2/s suggested by Prospero (1978) for horizontal scales of 100 km. Current velocities measured in Lake Michigan (Mortimer, 1971) also suggest that larger horizontal exchange coefficients may be appropriate. Perhaps recognizing this, MICH1 was calibrated with

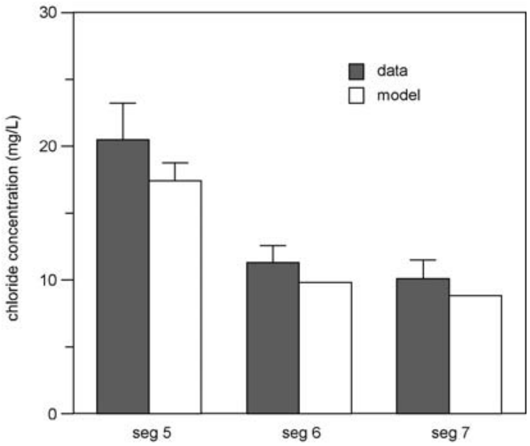


Figure 1.4. Results of chloride calibration of Green Bay dispersive exchange.

a large epilimnetic bi-directional flow. This flow, about eight times the outflow, was converted to an equivalent exchange of 1200 m^2/s in MICHTOX. Hypolimnetic horizontal exchange was increased to 40 m^2/s in MICHTOX, equivalent to outflow.

Exchange across the Straits of Mackinac was defined according to Quinn (1977), who estimated that bi-directional flow during stratification approximately doubled the outflow of Lake Michigan water. More recent measurements (Quinn, personal communication) indicate that the exchange may be considerably greater. Consideration of the bi-directional Straits of Mackinac flow, which produces a maximal outflow component of seven times the average discharge, reduces the northern Lake Michigan hydraulic residence time from seven years to less than four years.

1.4.4 Solids Balance

A solids mass balance was constructed for MICHTOX to simulate the particle transport fluxes of settling, resuspension, and burial in Lake Michigan. These appear as particle velocities in the toxic chemical mass balance equations. Although Great Lakes sediments represent a diverse particle assemblage, a single solid class representing fine-grained sediments was simulated in MICHTOX. Thus, no distinction between biotic and abiotic particles nor representation of particle aggregation were considered in this model. Sediment focusing was simulated by defining the area of each surficial sediment segment according to the extent of deposition zones in that portion of the lake.

The calibration of the solids balance was achieved by varying solids loading and resuspension velocities to match data for monthly average suspended particle concentrations M [M/L^3] in the surface water segments. Surficial sediment burial rates, thickness, and depositional fractions were based upon measured values listed, along with their sources, in Table 1.1. A constant settling velocity of 1.5 m/d was assumed, and sediment resuspension fluxes were constrained to maintain a constant sediment particle concentration of 240 kg/m^3. Finally, the epilimnion

Table 1.1. Sediment Segment Parameterization

Sediment Segment	Depositional Fraction	Burial Velocity (mm/y)	Mixed Layer Thickness (cm)	Mixed Layer Residence Time (y)
11	0.68[a]	1.7[c]	3.3[c]	20
12	0.59[a]	1.7[c]	3.3[c]	20
13	0.2[a]	0.63[d]	3.3[c]	53
14	0.32	20	10	5
15	0.5[b]	0.25[b]	9[b]	350
16	0.74[b]	0.25[b]	4[b]	160
17	0.31[b]	0.25[b]	4[b]	160

Sources: [a]Cahill, 1981; [b]Edgington, 1991; [c]Robbins and Eadie, 1991; [d]Robbins and Edgington, 1975 was isolated from resuspended particles during stratification. The resulting particle loads and resuspension fluxes, expressed as annual averages, are presented in Table 1.2. The resuspension fluxes vary inversely with water column depth, as expected for a process responding predominantly to wave action. The suspended particle calibration, for all water column segments, is displayed in Figure 1.5. Surface water suspended solids concentrations for Lake Michigan were reported by Robbins and Eadie (1991); concentrations in Green Bay were based upon the GBMBP cruise data (U.S. Environmental Protection Agency, 1989a). The "build-up" of suspended particle concentrations in the hypolimnion during stratification is consistent with the observed development of a nephloid layer near the lake bottom (Eadie *et al*., 1983).

Table 1.2. Particle Flux Parameterization

Segment	Depth	Resuspension Flux ($kg/m^2/d$)	Solids Load (kg/d)
1	75	2.2	2.5e7
2	55	1.7	2.2e7
3	36	5	4.2e6
4	2.2	38	4.3e5
5	5.9	13	-1.9e5
6	13	3.6	1.3e5
7	16	2.2	4.4e5

Because the surficial sediment is treated as completely-mixed in the mass balance, its volume V_s is properly defined by the thickness of the mixed sediment layer and the segment depositional area. The mixing of the surficial sediment is primarily the result of bioturbation. Dividing the mixed sediment layer thickness by the burial velocity determines the residence time of particles, and presumably of particulate chemical, in this well-mixed layer. The sediment segment also represents the reservoir of particles and particulate chemical available for resuspension. The sediment residence time controls the accumulation rate in the sediment mass balance, and resuspension of particulate chemical ties the long-term water column accumulation to this rate as

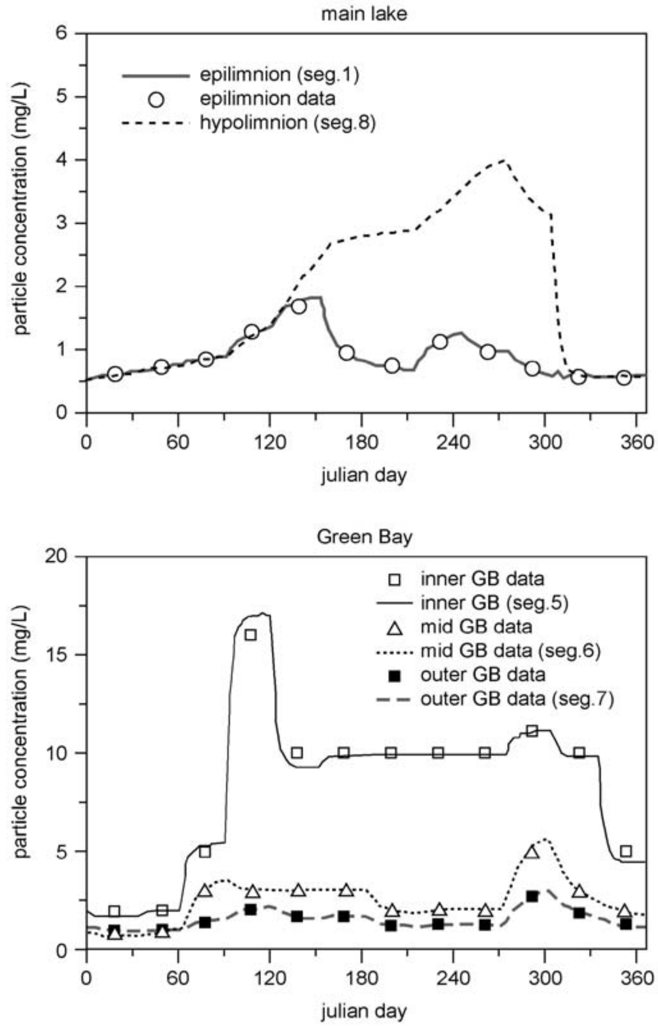


Figure 1.5. Suspended particle calibration.

well. Based upon the observed decline of particle-reactive radioisotopes in the Great Lakes, the mixed-layer residence time is approximately 20 years. The main lake surficial sediment thickness, 3.3 cm, was based upon this residence time. Radioisotope distribution in sediment cores from Lake Michigan suggest a mixed-layer thickness ranging from 1 to 2 cm based upon lead-210 (Edgington and Robbins, 1976) to 4 cm based upon cesium-137 (Robbins and Edgington, 1975). Extensive sampling of Green Bay sediments (Edgington, 1991) provide mixed-layer thicknesses of 9 cm (inner bay) and 4 cm (mid- and outer-bay). Surficial sediment mixed-layer depths and residence times used in the model are summarized in Table 1.1.

The model for HOC partitioning described below requires specification of the organic carbon fraction (f_{oc}) of particles, because organic carbon is considered to be the active sorbent for these chemicals. Based upon the data of Robbins and Eadie (1991), f_{oc} for particles in surface water was specified monthly (Figure 1.6) after correction to remove $CaCO_3$. Particle f_{oc} in the hypolimnion was specified as 30% of epilimnion values, based upon limited data from the same source. Considerable decomposition of particulate organic carbon occurs in the hypolimnion of Lake Michigan (Eadie *et al*., 1984). The f_{oc} for surficial sediment particles was assumed to be 3%; this value was based upon extensive surficial sediment characterization in Lake Ontario (Thomas *et al*., 1972).

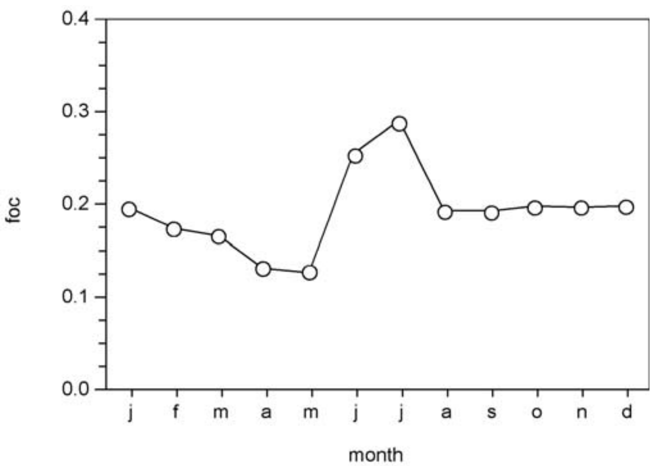


Figure 1.6. Organic carbon fraction of surface water particles.

1.4.5 Chemical Partitioning and Loss

1.4.5.1 Partitioning

Partitioning, which defines the distribution of chemical between dissolved and sorbent compartments, is a process of fundamental importance in determining the transport and fate of hydrophobic toxic chemicals. Model sorbent compartments for HOCs include the organic fraction of sediment particles and non-settling organic matter (NSOM), also referred to as colloidal organic carbon. Partitioning between phases is treated as a linear, reversible, and rapidly equilibrating process. Partitioning is represented in the mass balance formulations as fractions (f_d: dissolved; f_s: particle-sorbed; f_b: NSOM-bound) of the total chemical in each phase. Examination of the mass balance equations reveals that partitioning fractions appear throughout the model. Partitioning affects nearly all other processes in the mass balance model by (1) defining chemical fractions transported by particles, (2) defining the dissolved chemical fraction subject to volatilization, photolysis, and available for direct uptake by biota; and (3) defining mobile chemical fractions in sediment pore water.

Chemical fractions are determined by organic carbon sorbent concentrations and partition coefficients defining equilibrium chemical distribution between phases. The three-phase model developed to describe PCBs partitioning (Baker *et al*., 1986) was simplified and used in conjunction with a correlation relating the particulate organic carbon (POC) partition coefficient K_{oc} to the octanol-water partition coefficient K_{ow} (Eadie *et al*., 1990):

$$\log K_{oc} = 1.94 + 0.72 \log K_{ow}$$

The partition coefficient K_p is calculated from K_{oc} by:

$$K_p = r/c_d = f_{oc}\ K_{oc}$$

where:

$r = f_{sc}/M$ = sorbed (particulate) concentration of chemical $[M_{chem}/M_{sed}]$

$c_d = f_d\ c$ = dissolved concentration of chemical $[M_{chem}/L^3]$

f_{oc} = fraction organic carbon of particles

The three-phase model predicts that the observed distribution coefficient K_d for HOCs will be lower than the partition coefficient K_p due to the influence of NSOM binding:

$$K_d = \frac{r}{c_d + c_h} = K_p / (1 + f_c\ M K_p)$$

This formulation produces results comparable to the "particle effect" model of Di Toro (1985). The f_{oc} is an empirical parameter relating the efficiency of NSOM binding to that of particle sorption. Figure 1.7 displays how the dissolved chemical fraction

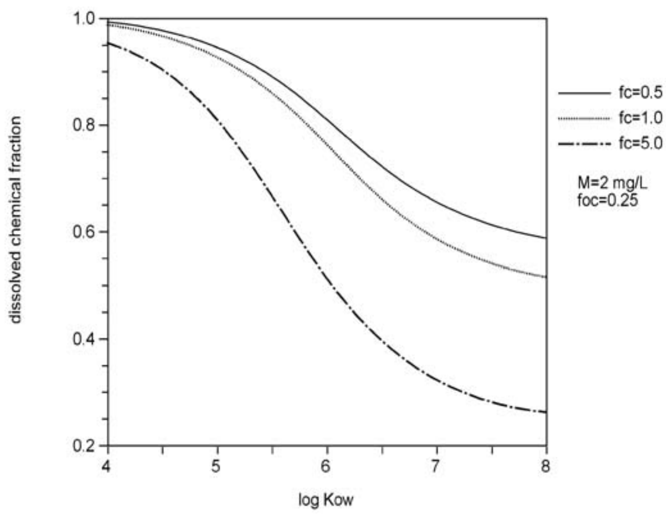


Figure 1.7. Partitioning model: Sensitivity of dissolved chemical fraction to non-settling organic matter binding efficiency.

varies according to K_{ow} for different values of f_c. The larger the value of f_c, the greater will be the reduction in dissolved fraction as hydrophobicity increases; if f_c equals one, a chemical will partition equally between particles and NSOM. This model has been calibrated to several sets of water column partitioning data from the Great Lakes; the results are shown in Figure 1.8. A f_c of 0.5 was used in MICHTOX. A similar approach was used to model partitioning in the surficial sediment. There, however, a NSOM binding efficiency based upon organic carbon was parameterized, based upon the data of Capel and Eisenreich (1990).

Lead and plutonium partitioning was defined for dissolved and particulate phases only. Data for lead-210 in Lake Michigan (Van Hoof and Andren, 1989) suggested a lead $\log K_p$ of 6.3. For plutonium, K_p was parameterized to reproduce a dissolved water column fraction of 80%, as reported for Great Lakes waters by Alberts and Wahlgren (1981). The particle effect model (Di Toro, 1985) was used to predict the expected decline in lead and plutonium partition coefficients with increasing suspended particle concentration.

1.4.5.2 Volatilization

Chemical exchange between air and water occurs by rainfall washout, dry deposition, absorption, and volatilization. Washout and deposition will be considered as loading terms to MICHTOX and are described later in this report. Absorption and volatilization may be combined as an expression for net volatile exchange:

$$k_v \left(f_{vA} \; c_A / H' - f_{dE} \; c_E \right)$$

the product of a volatilization rate k_v [L/T] and the gradient between atmospheric (f_{cA} c_A/H') and water column (f_{dE} c_E) chemical concentrations. Depending upon the direction of this gradient, net volatilization may represent either a source or sink of chemical. Applying the two-film theory (Whitman, 1923), volatilization rate becomes a function of serial mass transfer resistances in liquid and gas films at the air-water interface, with the overall rate constant given as:

$$k_v = \frac{1}{\dfrac{1}{K_1} + \dfrac{1}{K_g H'}}$$

where:

K_1 = the liquid film mass transfer coefficient [L/T]

K_g = gas film mass transfer coefficient [L/T]

H' = dimensionless Henry's constant defining chemical equilibrium between vapor and dissolved phases.

Henry's constant for each toxic chemical was either based upon direct measurement or, more often, calculated from solubility and vapor pressure data. Liquid and gas film transfer coefficients were extrapolated from reaeration and evaporation rates, which can be reliably estimated from correlations with environmental factors. The correlations of O'Connor (1983) and Liss (1973) were used in MICHTOX. Details of the volatilization rate computation are provided in Endicott *et al*. (1990). The model incorporated the effects of both spatial and temporal variation of water and air temperature, wind speed, and ice cover upon volatilization rate. The simulated variability of k_v with temperature and wind speed for pentachlorobiphenyl (PCB5) is plotted in Figure 1.9. k_v is fairly sensitive to both of these environmental factors. The higher August water temperature

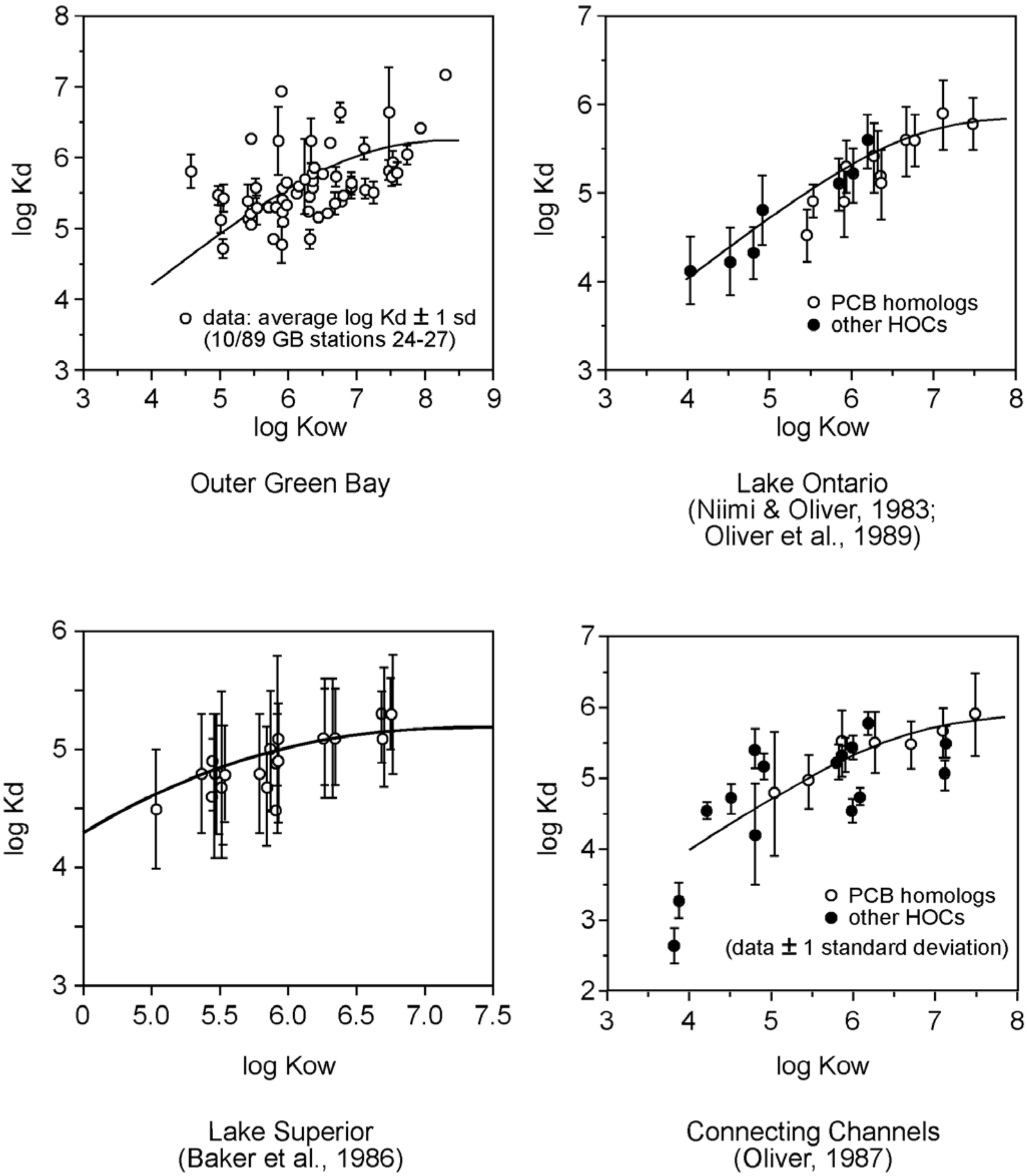


Figure 1.8. Calibration of partitioning model: Comparison to distribution coefficient data for HOCs in the Great Lakes.

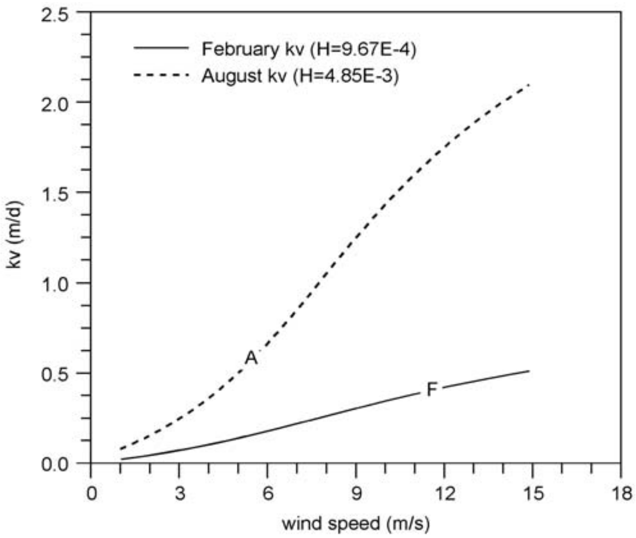


Figure 1.9. Sensitivity of computed volatilization rate to wind speed and temperature (pentachlorobiphenyl).

increases Henry's constant as well as the sensitivity of k_v to wind speed. Monthly average surface water temperature, over-lake air temperature, and wind speed were taken from Quinn (1977). Segment-specific ice cover was estimated from maps in the Great Lakes Ice Atlas (Assel *et al*., 1983).

1.4.5.3 Photolysis

Photolysis, a chemical reaction caused by the absorbance of light, was the only transformation process included in MICHTOX. Seasonal photolysis rate constants were calculated by the method of Zepp and Cline (1977) for BaP, HCB, and TCDD, while rates found in the literature were used for DDE and dieldrin. Photolysis was assumed to be insignificant for the other toxic chemicals except TCDF, based upon limited data (Mabey and Smith, 1982). No information regarding the photolysis of TCDF or other furans could be found in the literature; again, photolysis was assumed to be negligible.

1.4.5.4 Sediment-Water Diffusive Exchange

The final chemical transport process considered in MICHTOX is pore water diffusion between the surficial sediment and overlying water column. The diffusion process is considered to be a minor component of chemical sediment-water exchange, although data to confirm this are lacking. The diffusive exchange coefficient, K_f, is often estimated by the chemical free liquid diffusivity modified for pathlength tortuosity (Eisenreich *et al*., 1989). This produces a K_f of 0.1 to 1 cm/d, a range of values also suggested by Thomann and Mueller (1987). A K_f of 0.3 cm/d was used for all chemicals in the model. Although a single exchange coefficient is applied to both dissolved and bound chemical fractions in MICHTOX, K_f for NSOM-bound chemical is probably smaller.

1.4.6 Chemical Loads and Boundary Conditions

Chemical loads, including (but not limited to) atmospheric deposition and tributary loading, and boundary conditions with Lake Huron are forcing functions that control the mass balance model. Accurate temporal and particularly spatial resolution of loads is critical to successful model application. The present lack of reliable load estimates for many of the toxic chemicals fundamentally limits the development and application of mass balance models. It is primarily through efforts to measure and estimate chemical loads that other activities in support of the LaMP relate to mass balance modeling.

1.4.6.1 Atmospheric Deposition

Atmospheric deposition of chemicals occurs primarily by particle washout and dry deposition processes. The approach to estimating atmospheric deposition fluxes presented by Mackay and Paterson (1986) was followed in MICHTOX. Deposition flux F_{dep} [$M/L^2/T$] was calculated as the product of wet and dry deposition velocities and the air concentration of the chemical:

$$F_{dep} = (W_v G_r + v_{dry} \; f_{pA}) \, c_A$$

The volumetric washout ratio (W_v) is calculated as a function of Henry's constant, scavenging ratio (Q), the aerosol partition coefficient (K_{pA}), and the volumetric aerosol fraction (ϕ):

$$W_v = \frac{(1/H' + Q \, \phi \, K_{pA})}{1 + K_{pA} \, \phi}$$

The aerosol partition coefficient is, in turn, calculated from the chemical's liquid sub-cooled vapor pressure (P^S_L):

$$K_{pA} = \frac{6.0e + 6}{P_L^S}$$

Deposition parameterization followed values suggested as appropriate for the Great Lakes by Mackay (1989).

Air concentrations and deposition fluxes were treated as spatially uniform and (except for PCBs) constant in MICHTOX. The apparent spatial and temporal variability reported for both air concentrations and deposition processes suggests that this may be a poor assumption (Eisenreich *et al*., 1981; Hoff *et al*., 1992). Coupling MICHTOX to simulations of atmospheric chemical transport may be particularly valuable as a means to improve the realism and accuracy of this aspect of the model. For example, coupling water and air toxics models would allow simulation of the migration of PCBs from Green Bay to Lake Michigan or elsewhere in the Great Lakes *via* air transport.

Expected air concentrations and atmospheric deposition loads are presented in Table 1.3. These values and estimates of their uncertainty in terms of the lognormal coefficient of variation (lnCV), were selected based upon review of the literature and air monitoring data from the Michigan Department of Natural Resources (MDNR) (Moon, personal communication). TCDD concentrations have not been reported for ambient air; the expected value is one-third of the detection limit reported by Smith *et al*. (1990). It should be noted that the atmospheric deposition loads in Table 1.3 do not include absorption, which for some chemicals represents a large flux to the lake.

1.4.6.2 Tributary Loads

Tributaries convey toxic chemicals to the lake from a variety of sources including runoff, in-place pollutants, point source discharges, and ground water inflow. Present methods of estimating tributary loads rely upon frequent monitoring of flow and concentrations near the tributary discharge, an expensive and logistically-complicated effort. Tributary loading, particularly of hydrophobic chemicals including PCBs and lead, appears to occur predominantly during flood events. Such events must be sampled in order to accurately estimate in-place pollutants from tributaries into the lake; the likelihood of monitoring such events is, however, loads. Extreme events (such as a 50- or 100-year flood) could potentially transport huge quantities of extremely small. The data collection necessary to make reliable estimates of tributary loading of toxic chemicals to Lake Michigan has begun only recently

Table 1.3. Selected Air Concentrations and Calculated Atmospheric Deposition Loadings for Lake Michigan Priority Pollutants

Chemical	c_A (ng/m^3)	lnCV	Source	Atmospheric Deposition Loading (kg/y)
BaP	5.0e-3	0.41	Baker and Eisenreich, 1990	67
Chlordane	0.039	0.64	Hoff *et al*., 1992	47
DDT	0.030	0.61	Eisenreich *et al*., 1981	220
Dieldrin	0.032	0.64	Eisenreich *et al*., 1981	210
Heptachlor epoxide	0.016	0.64	Hoff *et al*., 1992	2.3
HCB	0.063	0.64	Hoff *et al*., 1992	4.4
PCB4	0.12	0.18	Hoff *et al*., 1992	83
PCB5	0.12	0.18	Hoff *et al*., 1992	340
TCDD	3.2e-5	0.64	Smith *et al*., 1990	0.38
TCDF	3.4e-4	0.64	Smith *et al*., 1990	3.6
Toxaphene	0.18	1.7	Rice *et al*., 1986	860

with the GBMBP. Approximately 300 samples were collected over a 17-month period to estimate loading of PCBs and lead from five tributaries to Green Bay.

1.4.6.3 Loading Histories

Because toxic chemical load estimation has not been a part of water quality surveillance efforts in Lake Michigan, the time history of loadings for only two toxic chemicals, plutonium and lead, could be reliably estimated. A more speculative loading history for PCBs was also estimated, based upon limited information.

1.4.6.3.1 Plutonium

Radioactive plutonium-239/240, a product of atmospheric bomb testing, has been monitored in the Great Lakes since 1970. A remarkable feature of plutonium is that its loading to the Great Lakes *via* atmospheric deposition is well-known (Robbins, 1985) due to measurements made at the Argonne National Laboratory. Additionally, the extent of plutonium partitioning to fine-grained sediments is similar to that for other hydrophobic toxic chemicals, and the only significant loss process for plutonium is sediment burial (radioactive decay may be neglected for the time scale of interest). These factors make plutonium an excellent state variable for calibration of MICHTOX. Robbins' plutonium deposition flux history is plotted in Figure 1.10. Plutonium deposition peaked in 1958-1959 and again in 1962-1964; values since 1980 have remained essentially zero.

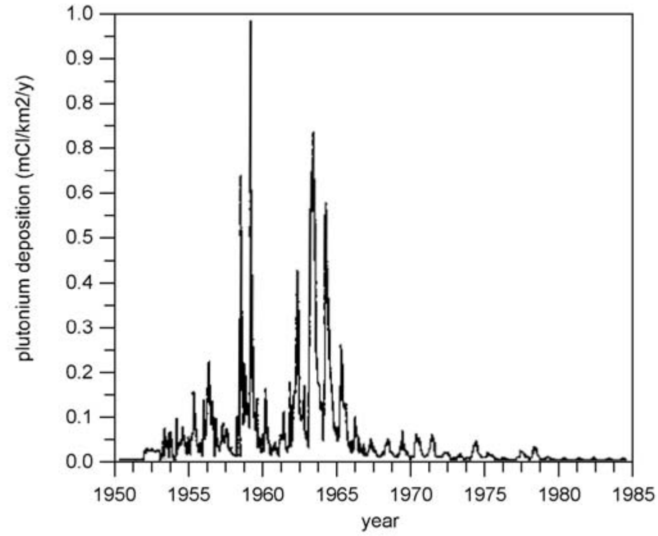


Figure 1.10. Plutonium deposition to Lake Michigan.

1.4.6.3.2 Lead

Lead has also entered the Great Lakes largely by atmospheric deposition. Regional lead deposition fluxes back to the 19th century were reconstructed from sediment records and coupled to recent atmospheric measurements (Edgington and Robbins, 1976). Tributary and other non-atmospheric sources were neglected in the estimation of lead loading. The resulting lead deposition history, converted to total Lake Michigan load and updated to the mid-1980s (Robbins, personal communication), is plotted in Figure 1.11. The decline in lead loading after 1970 coincides with the introduction of unleaded gasoline.

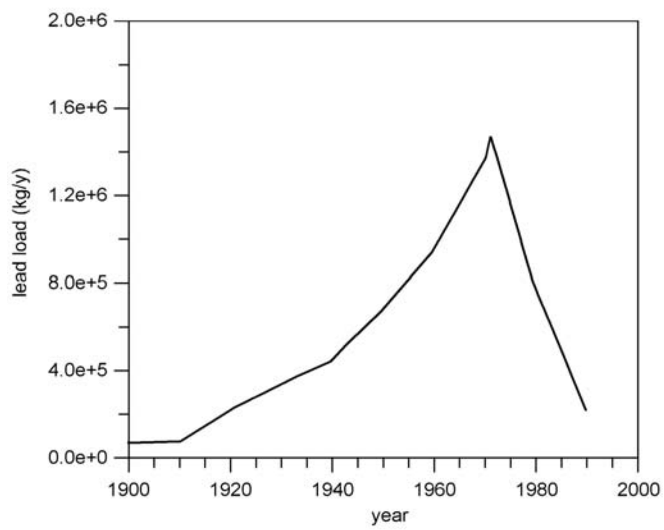


Figure 1.11. Total loading of lead to Lake Michigan.

1.4.6.3.3 PCBs

Polychlorinated biphenyls (PCBs) have been the most intensively monitored toxic chemical in both air and water in the Great Lakes. From the resulting data, numerous PCBs loading estimates have been made (Murphy and Rzesezutko, 1977; Rodgers and Swain, 1983; Thomann and Di Toro, 1983; Strachan and Eisenreich, 1988; Swackhamer and Armstrong, 1986; Mackay, 1989; Marti and Armstrong, 1990; Hermanson *et al*., 1991). Of these, Mackay's estimates for Lake Ontario are unique for they provide a continuous history of atmospheric, tributary, and point source loadings for PCBs. To adapt these estimates for use in MICHTOX, the magnitude of tributary loads was scaled to match the 650 kg/y estimated by Marti and Armstrong (1990) for Lake Michigan tributaries in 1980-1983. Atmospheric concentrations and deposition fluxes were also scaled to match the estimated average PCBs air concentration of 0.24 ng/m^3 in 1989. The resulting historical PCBs loading time-series is plotted in Figure 1.12 (point source loading was neglected in calculating total Lake Michigan PCBs load). The peak total loading in 1968 was estimated to be 7000 kg/y; 80% was contributed by atmospheric deposition. By 1990, the estimated total loading has declined to 640 kg/y, with the contribution of atmospheric deposition reduced to 40%.

This PCBs loading time-series was found to be in general agreement with other PCBs loading estimates for Lake Michigan (Figure 1.12), although the atmospheric deposition loads may be somewhat high. Further confirmation of the tributary loading function was provided by data analysis and mass balance model development for the lower Fox River as part of the GBMBP. The calibration of that model for the period 1989-1990 suggests a Fox River PCBs load of 160 kg/y. If the Fox River provides 50% of the total Lake Michigan tributary load of PCBs (as suggested by Marti and Armstrong, 1990) then the tributary load to the lake would be about 320 kg/y. This value is in acceptable agreement with the 1990 MICHTOX tributary loading value of 370 kg/y. Atmospheric deposition of PCBs was also measured as part of the GBMBP. Based upon these measurements, deposition to Green Bay was estimated as 2.5 to 22 kg/y (Franz and Eisenreich, 1991; Sweet and Murphy, 1991) with a best estimate of 11 kg/y. When extrapolated to all of Lake Michigan, this depositional load (32-280 kg/y) agreed fairly well with the loading time-series value of 260 kg/y.

1.4.6.4 Lake Huron Boundary Conditions

Toxic chemical concentrations in Lake Huron, a boundary condition to MICHTOX, were based upon 1986 average concentrations reported by Stevens and Neilson (1989). Because model results were found to be generally insensitive to this boundary condition, further resolution of Lake Huron concentrations was considered unnecessary.

1.4.7 Chemical Bioaccumulation

The MICHTOX bioaccumulation model was used to predict chemical accumulation up to lake trout in Lake Michigan. The bioaccumulation model was based upon the WASTOXv4 food chain model (Connolly and Thomann, 1985; Connolly, 1991). The model treats bioaccumulation as a chemical mass balance within individual organisms. The fundamental bioaccumulation equation for organism I of the food chain, consuming organisms j, is:

$$\frac{dv_i}{dt} = k_{ui}\, c\, f_d + \sum_{j=1}^{n} p_{ij}\, \alpha_{ij}\, C_{ij}\, v_j - K_j\, v_i$$

where the rate of chemical accumulation in the organism dv_i/dt equals the sum of direct uptake of chemical by the organism from water (k_{ui} c f_d) and the flux of chemical into the animal through feeding (p_{ij} α_{ij} C_{ij} v_j), balanced by chemical elimination (K'_i v_i). The parameters in the bioaccumulation equation are:

v_i = chemical concentration in organism I [M_{chem}/M_{wet}]

k_{ui} = uptake rate [$L^3/T/M_{wet}$]

p_{ij} = feeding preference factor ($\sum_{j=1}^{n} p_y = 1$) of organism I for organism j

α_{ij} = chemical assimilation efficiency across gut

C_{ij} = food consumption rate [$M_{prey,wet}/M_{pred,wet}$]

K'_i = chemical elimination rate [1/T]

The bioaccumulation equation is solved for time variable chemical concentration in individual age classes of each organism in the model. Bioaccumulation simulations were made for organisms residing in the southern Lake Michigan hypolimnion and sediment. Migration between segments was not considered in MICHTOX, although it could be added to the simulation. Migration could significantly impact bioaccumulation predictions for fish moving across large exposure concentration

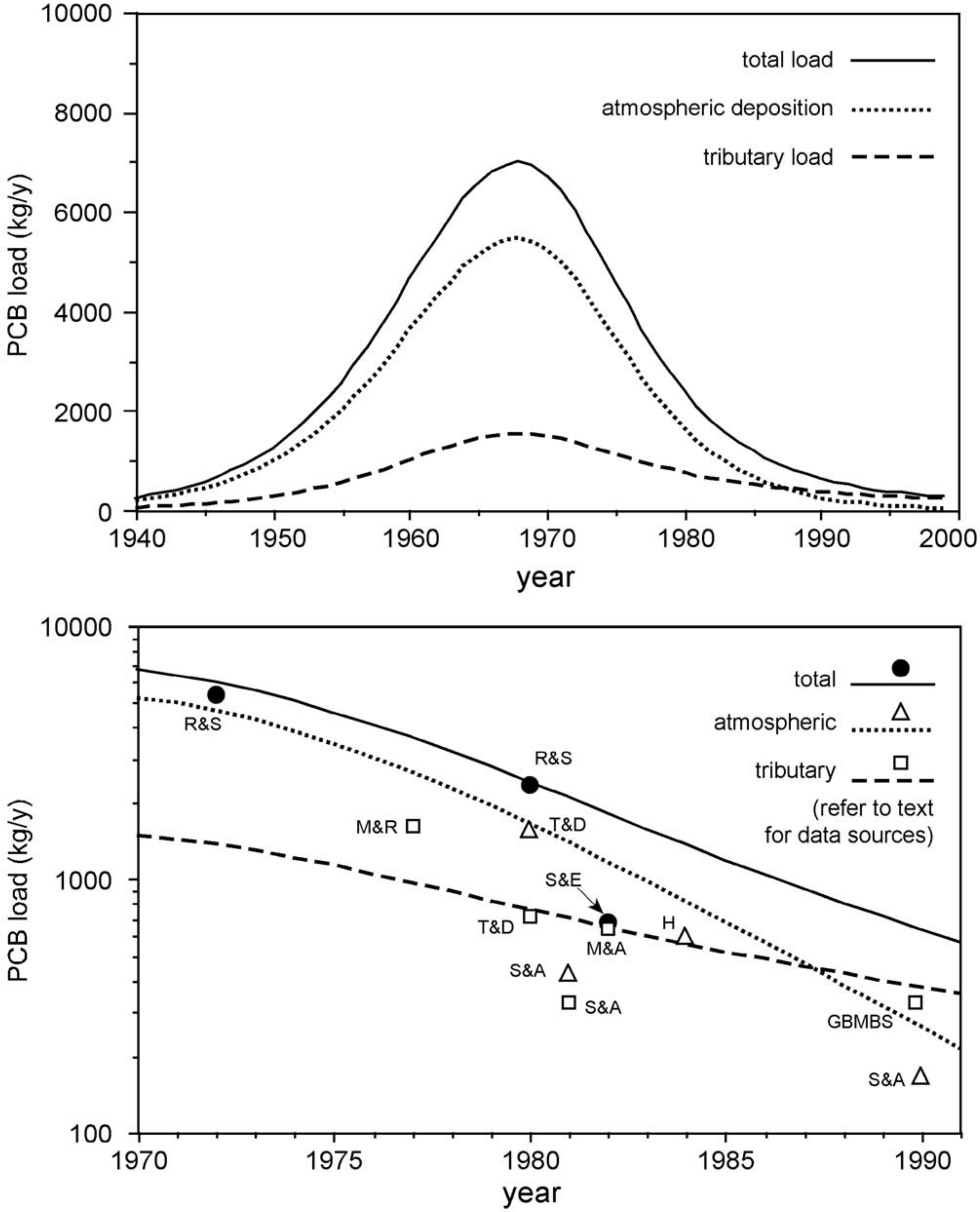


Figure 1.12. PCBs loading time function and comparison to reported PCBs load estimates.

gradients, most likely between open water and nearshore zones.

1.4.7.1 Food Chain

Trophic transfer (of both energy and chemical) was simulated by defining the feeding preferences expressed as diet fractions, p_{ij}, of all organisms in the food chain. Two alternative food chain structures, displayed in Figure 1.13, were defined for Lake Michigan lake trout. The first was the food chain developed by Thomann and Connolly (1984) to model PCBs accumulation in lake trout. This pelagic food chain of plankton, *Mysis*, alewife, and lake trout was constructed based upon extensive gut analysis data from the early 1970s. An alternative food chain incorporating linkage to benthos, in which trout consume bloater, was also constructed. This food chain structure was based upon the observation that bloater may have substantially replaced alewife as the major component of the adult lake trout diet in the deep, mid-lake reefs of Lake Michigan (Eck and Brown, 1990; Miller and Holey, 1991). This change in diet has apparently accompanied the reported decline of alewife since the late 1970s. Bloater were assumed to consume the benthos *Diporeia* and *Mysis*. This latter food chain may more accurately represent the current Lake Michigan lake trout trophic structure, although the data necessary to define all the feeding preferences in this food chain are lacking. For instance, the relative contribution of benthos to the bloater diet is unknown. However, simulation of the benthic-coupled food chain was considered important because benthos may accumulate significant concentrations of sediment-associated chemicals.

1.4.7.2 Uptake Rate

A number of assumptions must be made to relate the parameters in the bioaccumulation equation to properties of either the organism or the chemical. Particularly critical is the assumption that the variability in bioaccumulation between chemicals can be adequately parameterized as a function of K_{ow} (Thomann, 1989). This has been criticized because some data suggest that bioaccumulation varies according to chemical class as well as hydrophobicity. In MICHTOX, this assumption was modified to incorporate another chemical-specific bioaccumulation parameter, metabolization.

The rate of chemical uptake k_u, which parameterizes the transport of chemical across the gill, may be related to the respiration rate of the organism (R'):

$$k_u = \frac{E\,R'}{[O_2]}$$

where E is the efficiency of chemical transfer across the gill relative to oxygen, and $[O_2]$ is dissolved oxygen concentration $[M/L^3]$. Respiration was calculated by standard allometric relationships (Thomann and Connolly, 1984). As suggested by Thomann (1989), E was treated as a function of K_{ow} and organism size. E increases with chemical hydrophobicity, reaches a constant, maximum value at log K_{ow} of six, and then apparently declines.

1.4.7.3 Elimination Rate

Elimination represents the net loss of chemical from the organism by excretion, dilution by growth, and chemical metabolization:

$$K' = K + G + M_c$$

The chemical excretion rate K [1/T] can be calculated from the uptake rate and the bioconcentration factor (BCF) $[L^3/M]$:

$$K = \frac{k_u}{BCF}$$

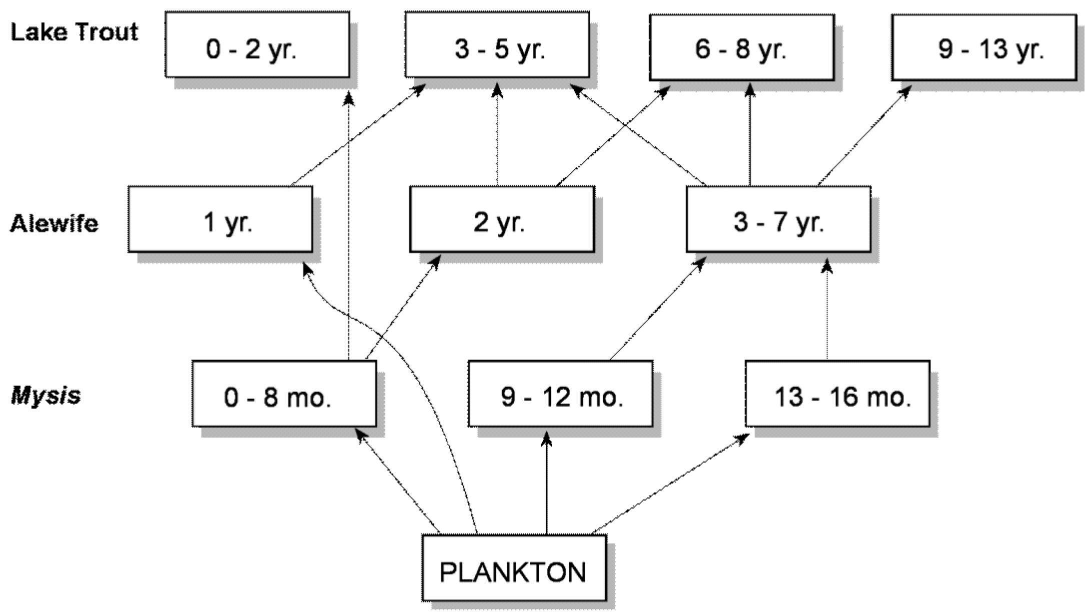
BCF, normalized by organism lipid content f_l $[M_{lipid}/M_{organism}]$ is approximately equal to K_{ow} at least up to log K_{ow} of six (Thomann, 1989):

$$BCF = f_l\,K_{ow}$$

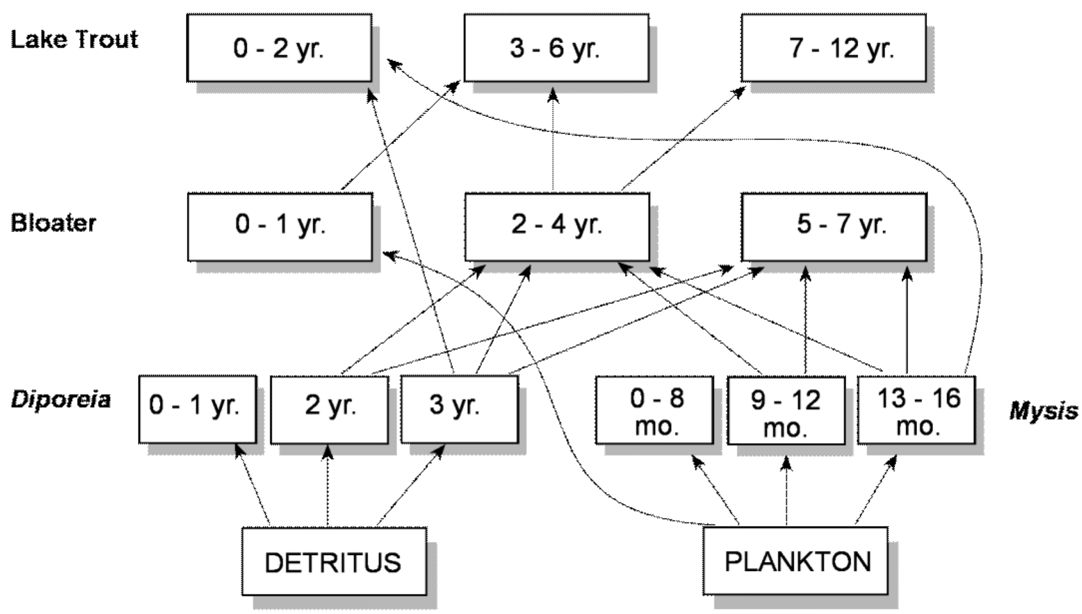
so that excretion rate may be calculated by combining these relationships:

$$K = \frac{k_u}{f_l\,K_{ow}}$$

The accuracy of this relationship for chemicals with log K_{ow} greater than six (including BaP, PCB5, and TCDD) is uncertain, as bioaccumulation data for such superhydrophobic chemicals are limited and often conflicting.



A. Pelagic Food Chain



B. Benthic / Pelagic Food Chain

Figure 1.13. MICHTOX food chain structure.

Growth rates G [1/T] were calculated from age-weight data of the individual species (Thomann and Connolly, 1984; Jobes, 1949; Evans and Landrum, 1989). The rate of chemical metabolism, M_c [1/T], was estimated for the three toxic chemicals metabolized by fish: BaP, TCDF, and TCDD. Lower trophic levels apparently do not metabolize BaP (Evans and Landrum, 1989); it was assumed they did not metabolize TCDF or TCDD either. Although M_c may be expected to vary with organism as well as chemical, adequate data for such specific model parameterization do not exist. Instead, constant rates of metabolism were parameterized for each chemical in fish. For BaP, a metabolization rate of 0.023/d was estimated from the bluegill sunfish data of McCarthy and Jiminez (1985). For TCDF and TCDD, the calibration of a bioaccumulation model to Lake Ontario trout data suggested a metabolization rate of 0.0035/d (Endicott *et al*., 1991). These metabolism rates correspond to chemical half-lives of 30 days for BaP and 200 days for TCDF and TCDD.

This calibration was based upon comparing the biota-to-sediment factor (BSF) for polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) to that for other HOCs. The order-of-magnitude decrease in BSFs for dioxins and furans were attributed to metabolization in fish, although other explanations for reduced accumulation of PCDDs and PCDFs have been offered (Oppenhuizen and Sijm, 1990). Reduced bioaccumulation of highly hydrophobic chemicals has also been suggested as evidence for metabolism of organophosphate pesticides (de Wolf *et al*., 1992). This procedure represents only a tentative calibration of metabolization; M_c would preferably be based upon direct measurement instead of inferred from an observed reduction in bioaccumulation relative to other chemicals of similar hydrophobicity.

1.4.7.4 Dietary Accumulation

Accumulation of chemical from food depends upon feeding preference, consumption rate, and chemical assimilation efficiency, the fraction of ingested chemical transferred through the gut to the organism. The rate of food consumption was calculated by the organism's energy requirements for growth and respiration, estimated by standard allometric relationships. Equating the caloric density to dry weight fraction (f_{dry}) of food consumption rates was calculated as:

$$C_{ij} = \left(\frac{f_{dry,i}}{f_{dry,j}}\right) \frac{G_i + R_i}{\alpha_i}$$

where α_i is the food assimilation efficiency [$M_{ingested}/M_{consumed}$]. A food assimilation efficiency of 0.8 was used for alewife and trout (Thomann and Connolly, 1984), while a lower value characteristic of herbivores, 0.4, was used for *Mysis*. Bloater food assimilation efficiency was 0.68, according to Rudstam *et al*. (1992). An α_i of 0.072 was selected for *Diporeia*, based upon consumption data (Dermott and Corning, 1988; Landrum and Robbins,1990).

Chemical assimilation efficiency was treated as a function of both species and chemical hydrophobicity. A chemical assimilation efficiency of 0.6 was used for trout and bloater based upon experimental data for PCBs assimilation in trout (Niimi and Oliver, 1983). For *Mysis* and alewife, the log K_{ow}-E relationship was found to also describe α_{ij} computed from HOC data for Lake Ontario (Oliver and Niimi, 1988), as displayed in Figures 1.14 and 1.15. The somewhat poorer fit for *Mysis* α_{ij} may be due to scatter in the plankton concentration data. A similar treatment of Lake Ontario *Diporeia* data was used to define a $\log K_{ow}$-α_{ij} relationship for that species; the result is presented in Figure 1.16. Regressing the PCBs congener data only, the following relationship was obtained for use in the model:

$$\log \alpha_{ij} = 5.49 - \log K_{ow} \;\; for \;\; \log K_{ow} > 5.49$$

$$(\alpha_{ij} = 1.0 \;\; for \;\; \log K_{ow} \le 5.49$$

Better parameterization of the chemical assimilation efficiency would be desirable, especially for benthos, because significant unexplained variability is apparent for this parameter.

1.4.7.5 Modeling the Base of the Food Chain

Bioaccumulating chemicals enter the pelagic and benthic food chains at the plankton and detritus, respectively. For plankton, chemical accumulation was assumed to be a partitioning process, so the plankton BCF_l was calculated from K_{oc} assuming 2%

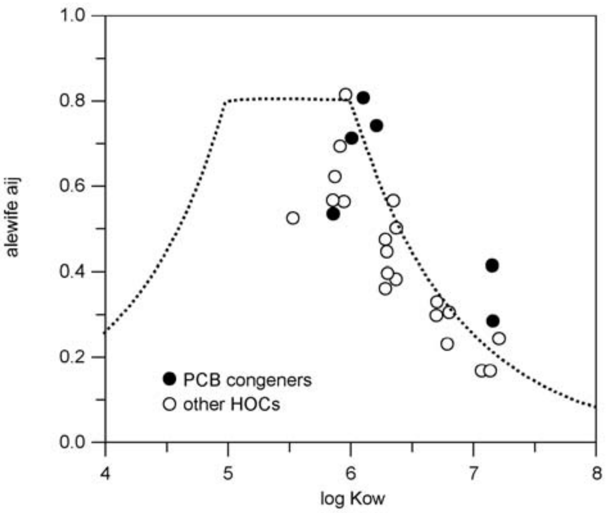


Figure 1.14. Chemical assimilation efficiency for *Mysis* calculated from Lake Ontario PCBs data.

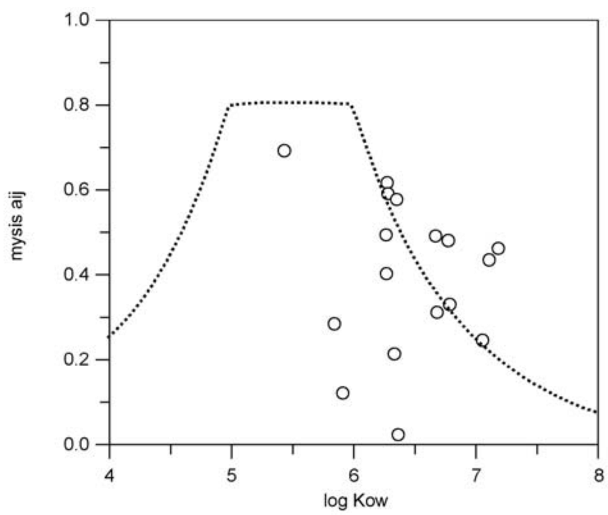


Figure 1.15. Chemical assimilation efficiency for alewife calculated from Lake Ontario HOCs data.

organic carbon (wet weight basis). The chemical concentration in detritus, the benthic food source, was assumed to be equal to that of the surficial sediment.

Neither plankton nor benthos accumulation is particularly well described by this model. Evidence that plankton accumulation is not simply a partitioning process has been presented by Skoglund and

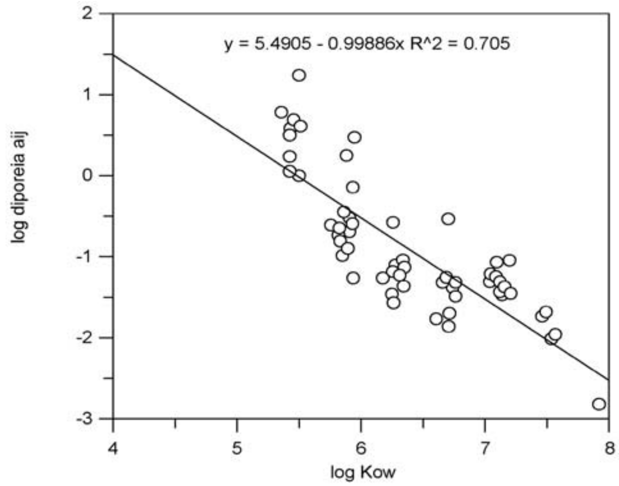


Figure 1.16. Chemical assimilation efficiency for *Diporeia* calculated from Lake Ontario PCBs data.

Swackhamer (1991). Also, the feeding of *Diporeia* is highly selective for fine, high organic carbon sediment (Landrum and Robbins, 1990) which may be enriched in HOC, thereby increasing contaminant accumulation above that being predicted by the model.

1.4.8 Steady-State Model

The solution of the mass balance and bioaccumulation equations simplifies considerably if the time derivative terms (d/dt) are eliminated. This steady-state solution of the model equations produces results which are adequate for many applications, except during periods of substantial concentration change. A steady-state version of MICHTOX was developed to validate the numerical computations in the dynamic model, and to facilitate model uncertainty analysis. The steady-state MICHTOX was implemented as a spreadsheet as well as a FORTRAN program; a sample of the spreadsheet output is shown in Figure 1.17. Solution of the steady-state mass balance equations is obtained by simultaneous solution of 14 linear equations, requiring the inversion of a matrix M of coefficients (Thomann and Mueller, 1987).

Several additional simplifications to the model were necessary to directly obtain the steady-state solution. Time variable model parameters were replaced by

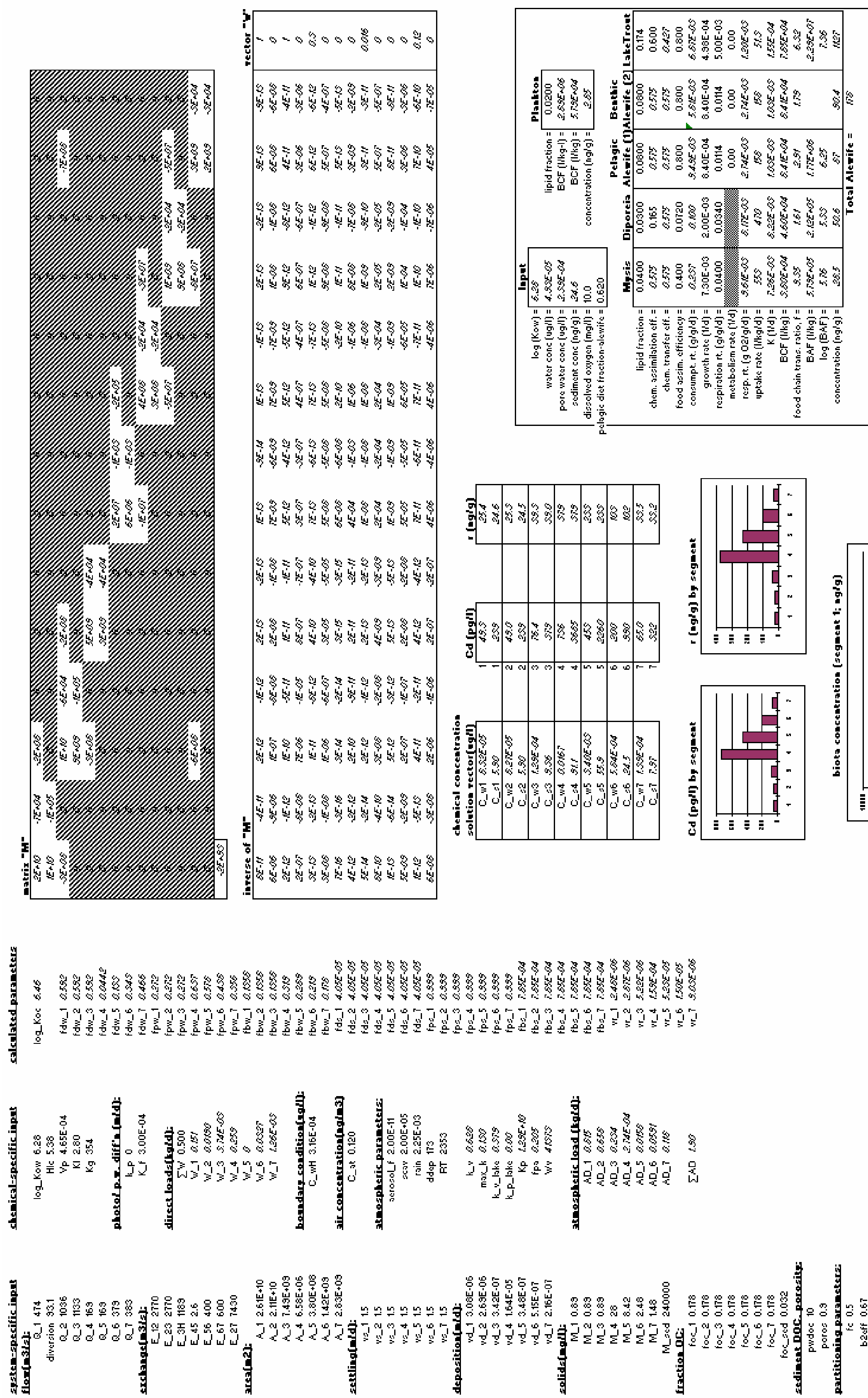


Figure 1.17. Steady-state spreadsheet model for pentachlorobiphenyl (PCB5).

annual-average constant parameters, and the seasonal stratification of the main lake water column was eliminated in favor of vertically-integrated segments. Volatilization and photolysis rates were adjusted to compensate for the missing influence of stratification on water column loss rates. The bioaccumulation model was also simplified, by adopting a simpler food chain structure (Figure 1.18). The alewife were assumed to consume 60% *Mysis*, a value based upon Flint's (1986) assessment of carbon flow in the Lake Ontario lake trout food chain. Alewife serves as a "generic" forage fish in this food chain, including other fish such as bloater, sculpin, and smelt.

Steady-state model solutions were compared to the equivalent dynamic model results to ensure consistency between models. For all chemicals, the steady-state model results were found to be within a factor of two of their dynamic model counterparts. Given the rather substantial simplifications to the dynamic model, this agreement with steady-state model results was considered acceptable. The alternative to developing a simplified steady-state model would be to run the dynamic model to steady-state, which was not feasible due to constraints upon computer resources.

1.4.9 Chemical-Specific Parameterization

Chemical-specific input parameters to MICHTOX include the octanol-water partition coefficient, vapor pressure, Henry's constant, the photolysis rate, and the rate of metabolism. These parameters, including sources of data, are summarized in Tables 1.4 through 1.7. Significant derived chemical parameters are tabulated as well. These tabulations also contain estimates of the uncertainty associated with the parameter values for use in model uncertainty analysis.

Parameterization was particularly difficult for the priority toxics representing chemical mixtures: chlordane, DDT, PCBs, and toxaphene. This difficulty arises because the parameterization must

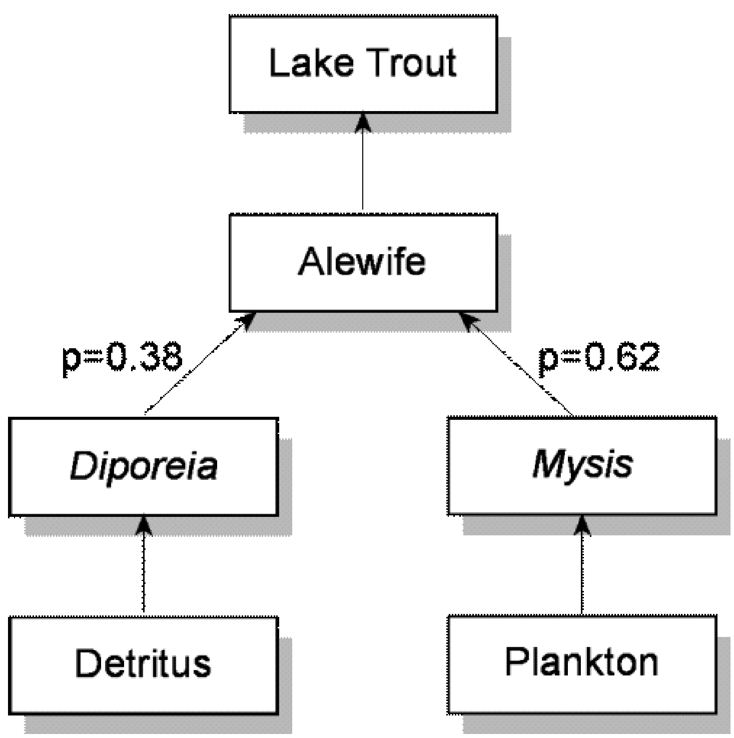


Figure 1.18. Simplified Lake Michigan lake trout food chain.

Table 1.4. Octanol-Water Partition Coefficient (K_{ow}) and Organic Carbon Partition Coefficient (K_{oc}) for Lake Michigan Priority Toxics

Chemical	log K_{ow}	lnCV of K_{ow}	Source	log K_{oc}
BaP	6.14	0.28	Endicott *et al*., 1990	6.4
Chlordane	6.00	0.69	Endicott *et al*., 1990	6.3
ΣDDT	6.00	0.49	Endicott *et al*., 1990	6.3
Dieldrin	5.50	1.0	Endicott *et al*., 1990	5.9
Heptachlor epoxide	5.40	0.66	Veith *et al*., 1979	5.8
HCB	5.84	0.49	Endicott *et al*., 1990	6.1
PCB4	5.89	0.28	Endicott *et al*., 1990	6.2
PCB5	6.28	0.31	Endicott *et al*., 1990	6.5
TCDD	7.02	0.31	Endicott *et al*., 1990	7.0
TCDF	5.82	0.66	Burkhard and Kuehl, 1986	6.1
Toxaphene	4.82	0.66	Lyman *et al*., 1982	5.4

Table 1.5. Physicochemical Parameters Used in Volatilization Parameterization of Lake Michigan Critical Pollutants

Chemical	P_y (Pa @ 10°C)	P_y lnCV	H_{hl} (Pa/M @ 10°C)	H_{lc} lnCV	Source
BaP	2.4e-6	0.64	0.013	0.64	Endicott *et al*., 1990
Chlordane	1.3e-3	0.64	1.3	0.64	Endicott *et al*., 1990
ΣDDT	1.1e-4	0.50	0.53	0.50	Endicott *et al*., 1990
Dieldrin	3.3e-4	1.0	0.028	0.98	Endicott *et al*., 1990
Heptachlor epoxide	5.1e-2	0.89	1.0	1.2	SCR*, 1988
HCB	2.8e-2	0.37	13	0.088	Endicott *et al*., 1990
PCB4	2.4e-3	1.1	6.3	0.78	Endicott *et al*., 1990
PCB5	4.7e-3	1.3	5.4	0.93	Endicott *et al*., 1990
TCDD	1.4e-5	0.78	0.45	0.40	Endicott *et al*., 1990
TCDF	3.5e-5	0.78	0.25	0.64	Rordorf, 1989
Toxaphene	3.3e-4	1.3	0.075	0.64	Sunito *et al*., 1988

*Syracuse Research Corporation

Table 1.6. Volatilization Rate Parameters for Lake Michigan Critical Pollutants

Chemical	K_l (m/d)	K_g (m/d)	K_y (m/d)
BaP	3.0	360	2.0e-3
Chlordane	2.7	340	0.17
ΣDDT	2.7	340	0.074
Dieldrin	2.7	330	4.0e-3
Heptachlor epoxide	2.8	350	0.14
HCB	3.1	370	1.2
PCB4	2.9	370	0.73
PCB5	2.8	360	0.63
TCDD	2.8	330	0.062
TCDF	2.8	330	0.034
Toxaphene	2.6	330	0.011

Table 1.7. Photolysis Rate for Lake Michigan Critical Pollutants

Chemical	kp (m/d)	kp InCV
BaP	1.4	(log -uniform over 0.64-3.0)
ΣDDT	0.068	1.7*
Dieldrin	3.6e-4	1.7
HCB	1.8e-3	1.7
TCDD	0.02	(log-uniform over 0.020 - 1.1)

*The 95% confidence limits are ± factor of 10.

properly average the properties of the chemicals in the mixture. Even if the constituent properties are known, averaging is difficult because the composition of the mixture may be variable or unknown. Model predictions for mixtures are particularly uncertain because the probability density functions for chemical-specific model parameters must account for variation amongst the properties of the constituents.

For DDT, the parameters determined for p,p'-DDD, -DDE, and -DDT were averaged; photolysis rate was based upon data for DDE. PCBs was modeled as two homologs, parameterized as average tetrachlorobiphenyl (PCB4) and PCB5. PCBs loads and air concentrations were assumed to be equally distributed between the two homologs, and PCBs model predictions were obtained by summing the PCB4 and PCB5 results. This approach was found to yield results almost identical to a more complicated procedure of modeling PCBs as six homologs, with loads defined according to an Aroclor-1248 homolog distribution. The mixture of polychlorinated terpenes that make up toxaphene probably have a range of parameters more variable than PCBs, yet data are available only for the technical mixture. Similarly, only limited data are available to parameterize chlordane, a mixture of *cis*- and *trans*-chlordane isomers, *trans*-nonachlor, and a variety of other chlordane-related chemicals.

1.5 Model Validation

Validation of predictions is necessary to judge the overall model performance and provides one indication of expected model accuracy. MICHTOX was validated by comparing model predictions to existing data for plutonium, lead, and PCBs in Lake Michigan. Additional validation of the bioaccumulation model was also performed. It should be noted that model parameterization included no direct calibration to toxic chemical data for Lake Michigan. Therefore, validation represents a "fair test" of the model's predictive abilities given the constraints of the data set.

1.5.1 Plutonium

The long-term prediction of plutonium concentrations in southern Lake Michigan is plotted in Figure 1.19. Also plotted in that figure is a long-term monitoring record for plutonium concentrations in the lake during unstratified periods (Robbins, personal communication). Plutonium concentrations are given in femtocuries per liter (fCi/L), a measure of radioactivity. The predicted seasonal divergence of epilimnion and hypolimnion simulations will be considered further. However, the simulated plutonium concentrations converge at fall overturn, and the agreement between model predictions at such a time with the long-term data is excellent. Because the singular loss mechanism for plutonium is sediment burial, this long-term agreement validates the main lake particle flux parameterization of MICHTOX.

Because the hypolimnion is seasonally isolated from the epilimnion due to stratification, concentrations in the two water column segments diverge during the summer of each year. This divergence is particularly apparent in the MICHTOX simulation after 1965, when plutonium loading had significantly declined. This portion of the simulation is plotted in greater detail in Figure 1.20 along with seasonal epilimnetic data (Wahlgren *et al*., 1977). From this period through the end of the simulation, the major source of plutonium entering the water column is resuspended sediment. Plutonium "builds up" in the hypolimnion during stratification as sediments resuspend and particle concentrations increase. At the same time, plutonium is depleted in the epilimnion because resuspended particles are trapped in the segment below. Residual atmospheric loading (which peaks each summer) and entrainment prevent plutonium from disappearing entirely from the epilimnion, however (Robbins and Eadie, 1991). At fall overturn, vertical particle fluxes quickly re-establish uniform water column plutonium concentrations. MICHTOX adequately simulates the magnitude of the epilimnetic depletion, although the prediction is out of phase in some years. This is because the seasonal representation of stratification in MICHTOX is somewhat inaccurate and does not vary year-to-year as does the lake. However, this agreement generally validates the simulation of the stratification's impact upon particle and particle-associated contaminant fluxes.

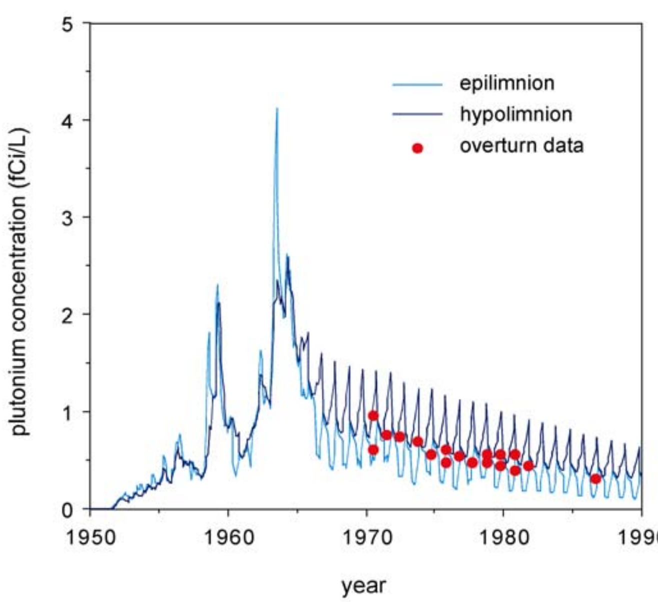


Figure 1.19. MICHTOX simulation of plutonium in southern Lake Michigan (epilimnion, hypolimnion, and overturn data).

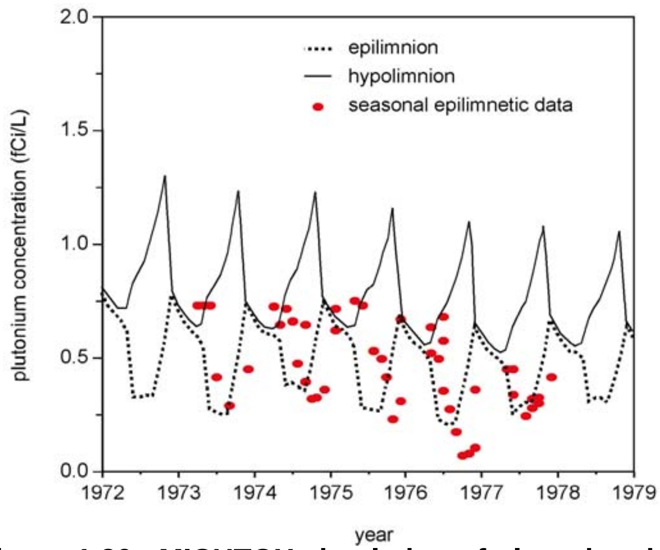


Figure 1.20. MICHTOX simulation of plutonium in southern Lake Michigan (epilimnion, hypolimnion, and seasonal epilimnetic data).

The variation of chemical concentrations in the lake water exhibited for plutonium should be expected for the other toxic chemicals as well, although substantiating data are not known to exist. Previous mass balance models for toxic chemicals in the Great

Lakes have utilized a vertically-integrated (completely-mixed) water column, assuming that the impact of stratification upon, at least, long-term simulations would be negligible. MICHTOX plutonium simulations suggest this may not be correct. Figure 1.21 displays a comparison of plutonium predictions made both with and without a stratifying water column. All other parameters and forcing functions were common to both simulations. The effect of stratification is seen to be a persistent elevation in water column concentrations following load reduction. Because this increases the simulated persistence of the chemical, it appears important to incorporate stratification in fate and transport models for, at least, Lake Michigan.

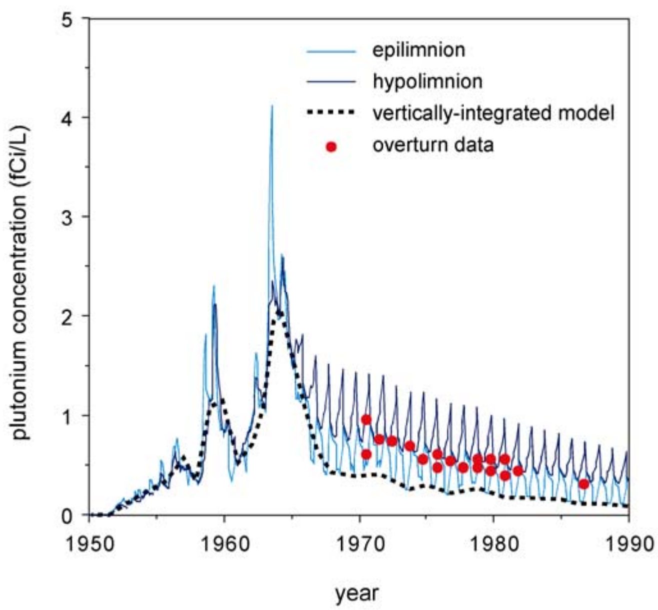


Figure 1.21. MICHTOX simulation of plutonium in southern Lake Michigan – sensitivity to vertical segmentation.

1.5.2 Lead

Lead, like plutonium, is a toxic chemical subject to loss by burial. The prediction of annually-averaged lead concentrations in southern Lake Michigan is plotted in Figure 1.22. Problems with analytical detection limits and sample contamination have confounded efforts to monitor lead as well as other trace metals in Great Lakes water; only the data reported by Rossmann and Barres (1988) is considered reliable. The reported concentration of

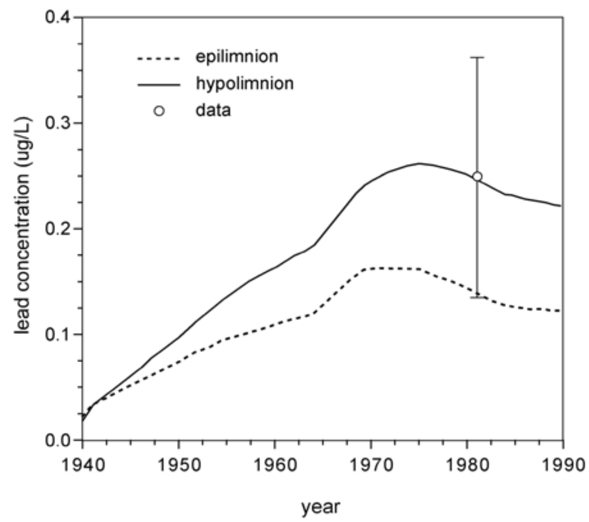


Figure 1.22. Simulation of annual-averaged lead concentrations in southern Lake Michigan.

lead in Lake Michigan, 0.25 µg/L, is in good agreement with the MICHTOX prediction. The simulation indicates essentially a "plateau" in lead concentrations since the early 1980s. The prediction for lead in southern Lake Michigan surficial sediment is plotted in Figure 1.23. Mudroch and Williams (1989) reports lead concentrations in Lake Michigan surficial sediment of 10 to 130 ng/g, with a mean value of 40 ng/g. The MICHTOX simulation is in the range of this data; however, the model overpredicts the mean value.

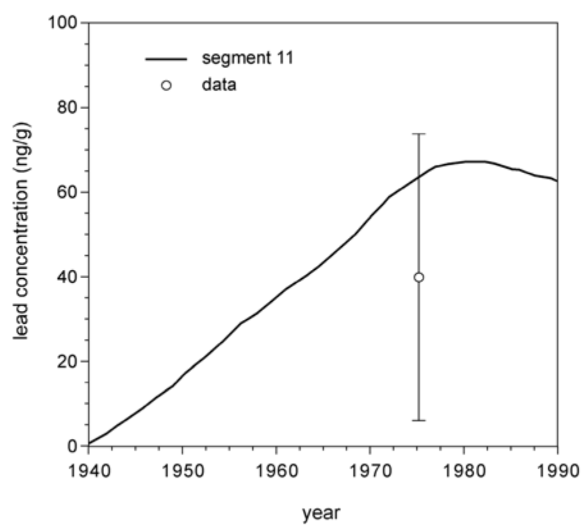


Figure 1.23. Lead simulation in southern Lake Michigan surficial sediment.

1.5.3 PCBs

A relative wealth of concentration data exists for PCBs in Lake Michigan, at least in comparison to the other priority toxics. However, this is an insufficient database to quantitatively compare with model predictions, which represent average concentrations over relatively large areas of the lake. Thus, only qualitative comparison to data was used to validate model predictions in water, sediment, and biota.

1.5.3.1 Water

The verification simulation for PCBs was made with the PCBs loading history described previously; unless otherwise noted, results are annual average predictions. Water column PCBs predictions are plotted in Figures 1.24 and 1.25 along with data for comparison. The southern lake simulation in Figure 1.24 indicates peak water column concentrations of 3.4 (hypolimnion) and 2.2 ng/L (epilimnion) in 1970, with values dropping to less than 0.6 ng/L by 1990. These predictions are in agreement with the data of Rodgers and Swain (1983; <10 ng/L in 1970, 3-9 ng/L in 1976) as well as the 1980 data of Swackhamer and Armstrong (1987). This latter data suggests a variance between epilimnetic and hypolimnetic PCBs concentrations (1.2 versus 1.7 ng/L) similar to the MICHTOX predictions (1.0 versus 1.8 ng/L). Central lake simulations are essentially the same; however, simulated PCBs concentrations in the northern lake segments are higher. At the 1970 peak values, northern lake concentrations are 30% higher than in the southern and central lake segments. Swackhamer and Armstrong's data show no such PCBs concentration increase in Lake Michigan, although none of the stations sampled were actually in the northern basin as defined in MICHTOX. Several factors could contribute to a problem in the northern basin, including insufficient data to characterize particle fluxes and concentrations, and overestimation of air concentrations and atmospheric fluxes over the northern lake.

Predicted PCBs concentrations in the three Green Bay segments are plotted in Figure 1.25, indicating a strong and persistent concentration gradient between inner- and mid-outer segments.

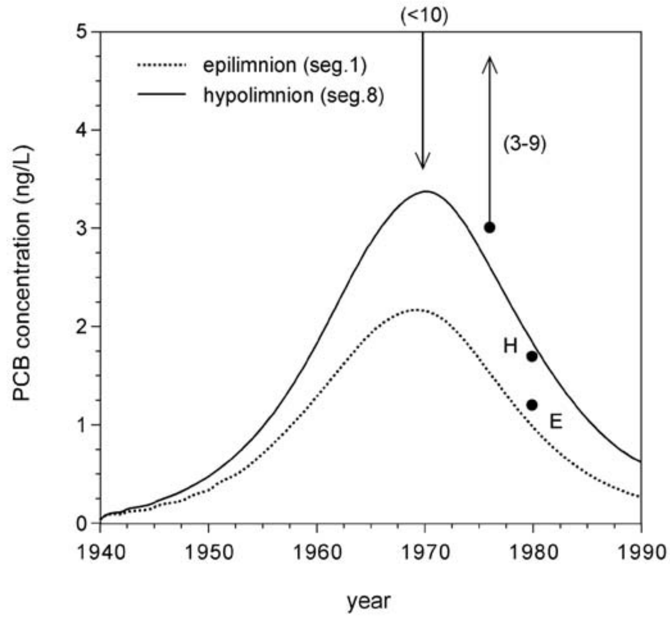


Figure 1.24. Simulation of PCBs in southern Lake Michigan.

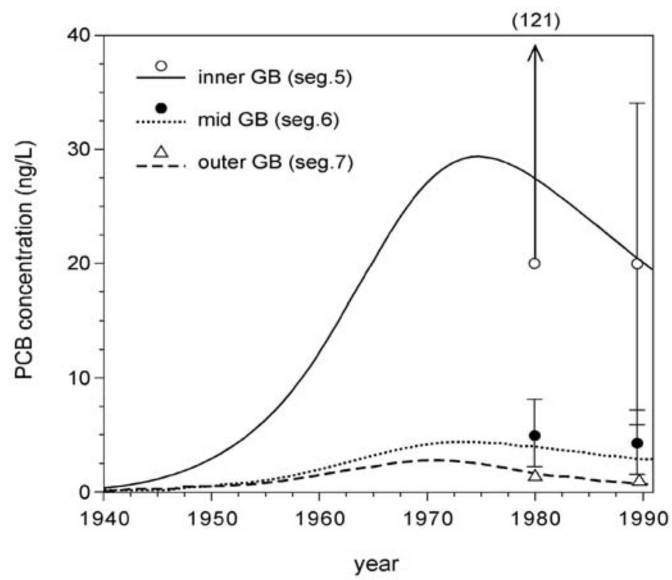


Figure 1.25. Simulation of PCBs in Green Bay.

Again, the PCBs predictions are in good agreement with water column data for 1980 (Swackhamer and Armstrong, 1987) and 1989 (GBMBP, October 1989 cruise). Simulated PCBs concentrations in the outer bay are compared to the main lake predictions in Figure 1.26, indicating a PCBs water concentration gradient of 0.5 ng/L between the two segments.

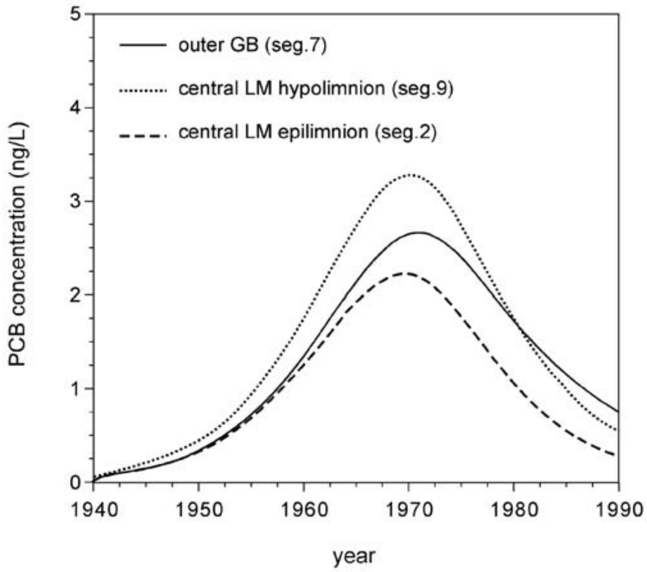


Figure 1.26. PCBs simulations in central Lake Michigan and outer Green Bay.

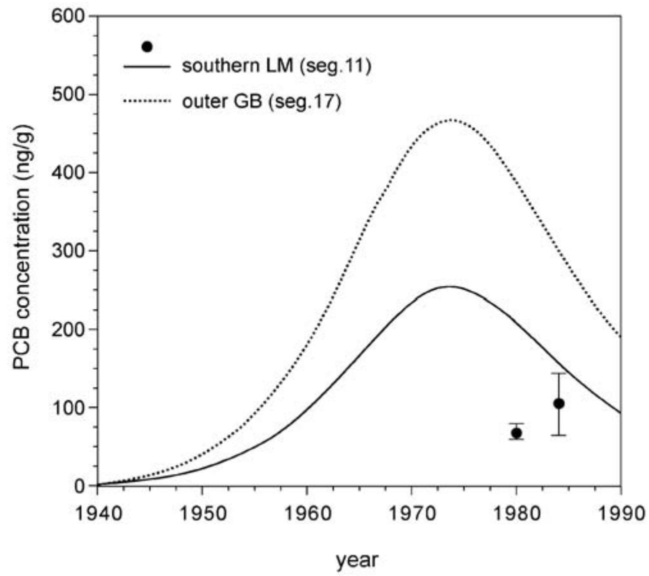


Figure 1.27. PCBs simulations in Lake Michigan and outer Green Bay surficial sediments.

1.5.3.2 Sediment

Verification of sediment concentration simulations is made difficult by spatial sediment variability which has generally not been adequately sampled. This should be partially resolved by the sediment sampling conducted during the GBMBP. Unfortunately, these data were not available at the time of this report. Simulated PCBs concentrations in surficial sediment segments are plotted in Figures 1.27 and 1.28. The southern lake simulation in Figure 1.27 indicates peak surficial sediment concentrations of 260 ng/g in 1974, with values dropping to 100 ng/g by 1990. Concentrations predicted for 1980 are consistent with the <200 ng/g reported by Sonzogni and Simmons (1981), Strachan and Eisenreich (1988), and Weinenger *et al*. (1983). Predicted sediment concentrations in inner- and mid-Green Bay (Figure 1.28) are much higher; peak inner bay sediment concentrations of 1900 ng/g are predicted for 1978. The predictions are again similar to sediment concentrations measured in the early 1980s (Swackhamer and Armstrong, 1988; Hermanson *et al*., 1991).

The vertical distribution of PCBs concentrations in sediment beneath the surficial mixed layer can be obtained from the time-series of surficial concentrations, by transforming the time scale to the sediment depth using the particle burial velocity. This transformation assumes that particles are buried without mixing beneath the surficial layer, and burial velocity (i.e. sedimentation rate) is constant. While these assumptions may be questionable, they are routinely made when sediment cores are radiometrically dated. A simulated sediment PCBs

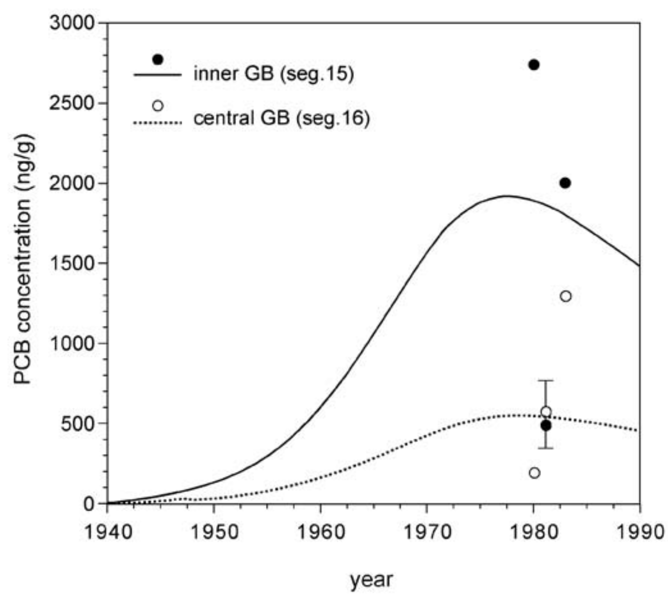


Figure 1.28. PCBs simulations in Green Bay sediments.

profile for southern Lake Michigan, corresponding to an "average" depositional zone sediment core collected at 1990, is shown in Figure 1.29. A pronounced concentration maximum beneath the surficial mixed layer is predicted; such a PCBs concentration distribution has been reported for several sediment cores collected in Lake Michigan (Hermanson and Christensen, 1991). However, comparison of other aspects of the sediment distribution to data is difficult. For instance, PCBs concentration profiles have apparently not been reported for sediment cores with sedimentation rates as high as the 400 g/m^2/y parameterized for southern Lake Michigan.

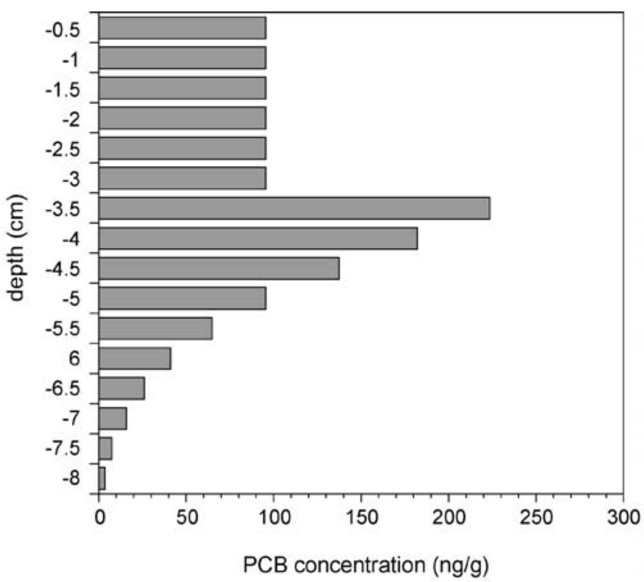


Figure 1.29. Simulated PCBs distribution in southern Lake Michigan sediments.

1.5.3.3 Biota

MICHTOX bioaccumulation model predictions for PCBs were validated using lake trout and bloater data. Lake trout monitoring has taken place since 1971, and a number of data sets have been compiled which document PCBs and other HOC levels in Lake Michigan fish. Several of these data sets are presented in Figure 1.30. The (age class) compiled age seven data were based upon USEPA STORET and other sources (Thomann and Connolly, 1984); the USEPA/USFWS data is from an ongoing federal monitoring effort (DeVault *et al.*, 1986). These data both show peak PCBs concentrations of 18 to 23

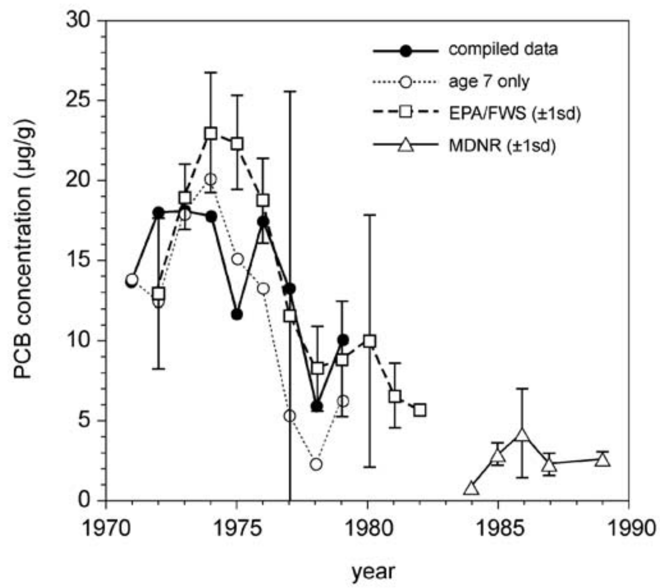


Figure 1.30. PCBs concentrations in Lake Michigan lake trout.

µg/g (ppm) occurring in 1974 followed by a fairly rapid decline; however, details of the time-series vary between data. More limited, recent data were obtained from the State of Michigan (Michigan Department of Natural Resources, 1990) which indicate that PCBs concentrations have leveled off at about 3 µg/g. The MICHTOX predictions of age seven lake trout PCBs concentrations are plotted with these data in Figure 1.31. Age seven was chosen because this age class is represented in all data sets. The model predictions are similar to the magnitude of PCBs concentrations measured in fish through 1980, although the distinct "peak" in PCBs concentrations around 1974 (particularly evident in the USEPA/USFWS data) is not reproduced. After 1980, the predicted PCBs concentrations, although declining, are higher than the data by a factor of two. In general, the predicted PCBs concentration trend is considerably less "dynamic" than that of the data.

Three factors may be suspected as causes of the lack of fit of the trout PCBs predictions. First, errors in the model structure and/or parameterization may be responsible. The dynamics of the trout PCBs predictions follow the concentration change in the sediment; this aspect of the model simulation will be considered later in the report. Alternatively, the loading time-series for PCBs to Lake Michigan may be in error. If PCBs loading declined more rapidly

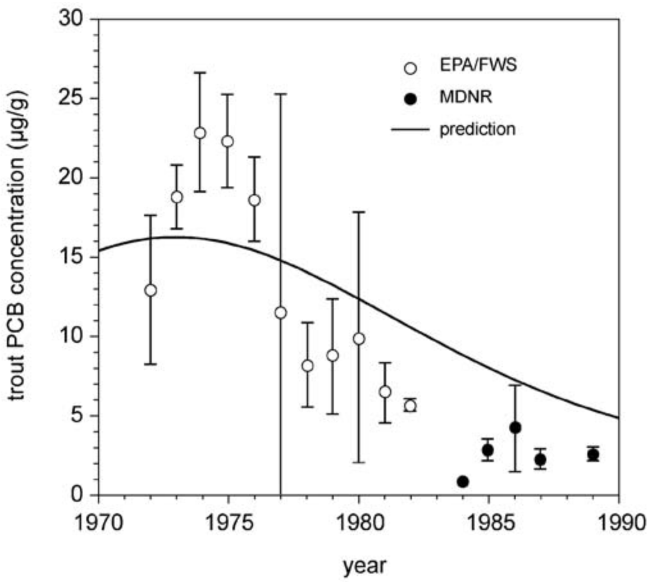


Figure 1.31. Verification of PCBs accumulation in age seven lake trout.

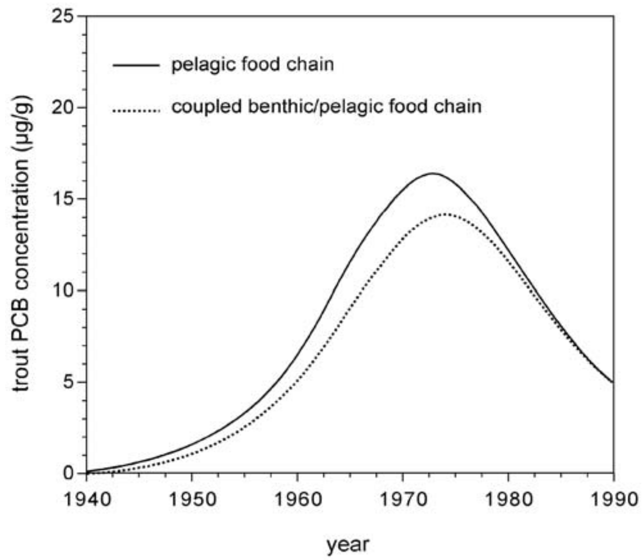


Figure 1.32. Sensitivity of trout PCBs predictions to the food chain.

than the estimated time-series after 1970, then PCBs concentrations throughout the model, including trout, would also decline at a rate more consistent with the data. Presently, it is not possible to distinguish between these possibilities as the source of lack of fit. Finally, the quality of the data may be questioned. The reliability of PCBs concentration data generated during the early 1970s has been repeatedly questioned because of concerns with quantification errors due to interference with other chemicals such as DDT and toxaphene which coelute in GC chromatograms (Swackhamer and Armstrong, 1987). Both data sets used packed column GC for analysis, with results quantified as Aroclors; however, comparability of the analytical results cannot be directly evaluated. The two data sets plotted together may not be homogeneous, either. The USEPA/USFWS data were based upon fish collected from a single Lake Michigan location (off Saugatuck, Michigan). In comparison, the MDNR data are for relatively small sample sizes collected at a number of southern Lake Michigan locations.

Simulated trout concentrations for both pelagic and benthic/pelagic food chains are plotted in Figure 1.32. Predicted trout bioaccumulation for the coupled benthic-pelagic food chain lags the prediction for the pelagic food chain, and benthic coupling lowers trout concentrations. This is contrary to the expectation that a benthic food chain linkage would result in greater bioaccumulation. At steady-state, higher trout concentrations are predicted for the benthic-coupled food chain; however, this condition does not occur in the dynamic simulation. This discrepancy relates, in part, to the dynamics of benthic versus pelagic exposure concentrations. Sediment PCBs concentrations, which provide the additional chemical exposure to the benthic-coupled food chain, lag significantly behind the water column concentrations. Polychlorinated biphenyl loading significantly declines before sediment concentrations approach steady-state with the maximum load; this "hysteresis" is reflected in the bioaccumulation predictions. Because the pelagic-based food chain results better match the data, they will be presented as dynamic model results for the remainder of this report.

Simulated PCBs concentrations in other age classes of lake trout were also verified. Age class simulations are plotted with data for 1971 (Thomann and Connolly, 1984) in Figure 1.33, indicating very good agreement except for ages two and three. A number of explanations have been offered for the lack of fit for young trout, including problems with age classification of fish based upon age-weight relationships, the impact of reproduction on chemical concentrations, and different (higher) exposure

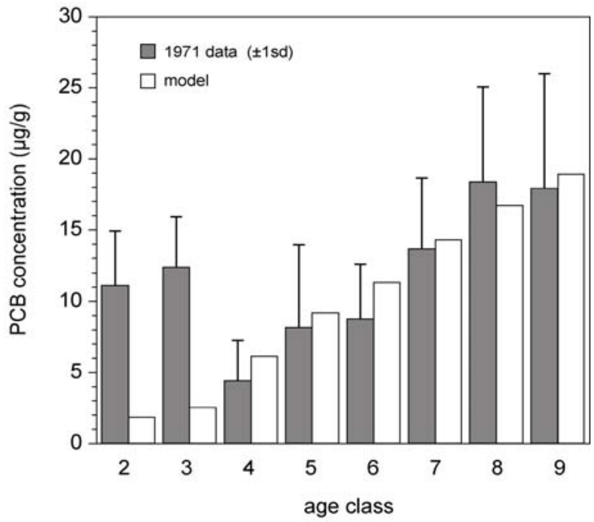


Figure 1.33. Verification of PCBs accumulation predictions in lake trout age classes 2-9.

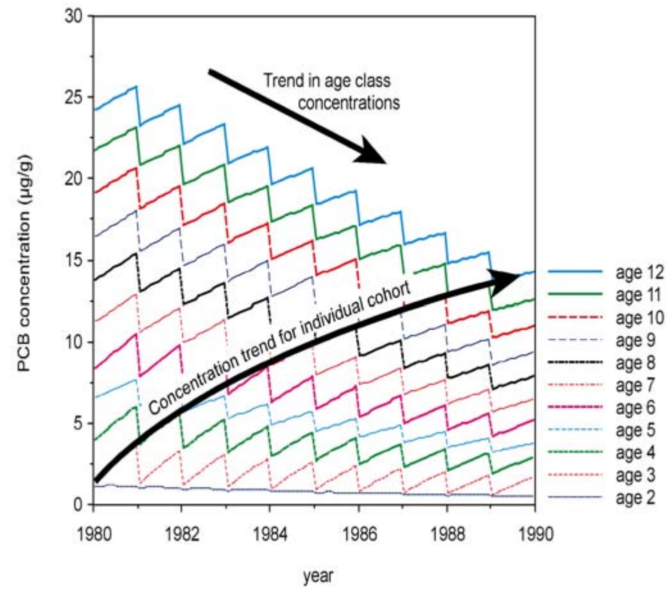


Figure 1.35. Simulation of PCBs concentrations in age 2-12 trout, 1980-1990.

environments for young versus adult trout. The annual simulation of age two through 12 trout for the period 1980-1990 is plotted in three dimensions in Figure 1.34, showing the decline in PCBs concentrations for all age classes of fish over that period. Figure 1.35 displays the same model simulation on a finer time scale; although the trend in PCBs age class concentrations is downward, the concentration for an individual trout cohort over this period is still increasing. According to Thomann (1989), the variation between age classes of fish

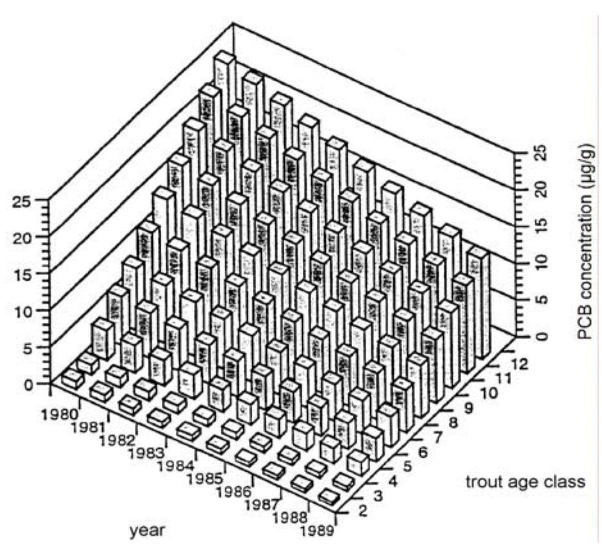


Figure 1.34. Simulation of PCBs concentrations in age 2-12 trout, 1980-1989.

largely disappears when chemical concentrations are normalized by lipid content. This was the justification used to simplify the steady-state model to predict only a single concentration in trout.

The predicted PCBs concentration in bloater is plotted with available data (Hesselberg *et al*., 1990) in Figure 1.36. Because both lipid content and size (and presumably age) of the collected bloater have substantially declined through time, the concentrations were normalized for lipid content. The agreement of model predictions with these data is good; in fact, the prediction matches the bloater PCBs concentrations exactly in the early 1970s, and again in the mid-1980s. Between these periods, predicted concentrations decline gradually, while the data show a rapid concentration drop followed by a gradual increase after 1980. As discussed by Hesselberg, the dynamics of PCBs bioaccumulation in bloater may be driven more by ecological stress than by chemical exposure. Given that MICHTOX simulates a fixed food chain structure and constant parameterization of consumption and growth, such factors cannot be accommodated in the simulation. However, the general agreement with the bloater PCBs data validates the benthic coupling of the bioaccumulation model because bloater consume *Diporeia* as well as *Mysis*.

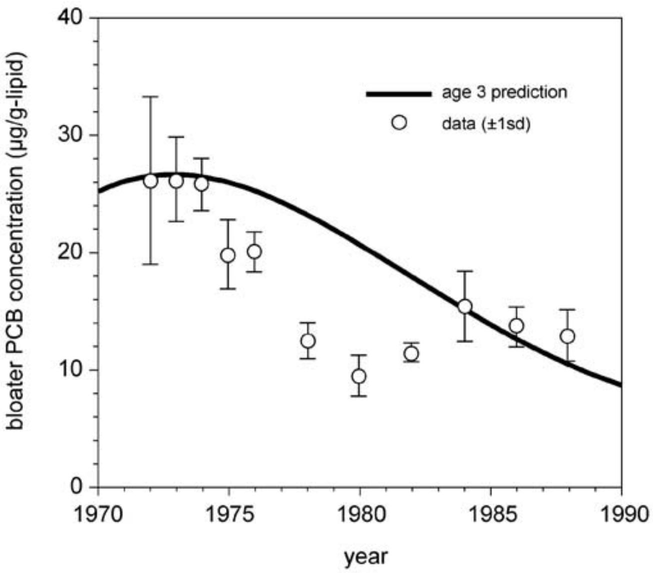


Figure 1.36. Verification of PCBs concentration predictions for bloater.

The validation of MICHTOX using PCBs data was considered to be successful based upon the qualitative agreement between model and data. Because the available data were inadequate to calculate average concentrations consistent with model state variables, no quantitative or statistical validation was possible. In particular, differences in concentration trajectories for trout suggest a need for improvement of this aspect of model predictions. This suggestion will be pursued later in the report.

1.5.3.4 Bioaccumulation

Toxic chemical data to validate bioaccumulation simulations at all trophic levels and for chemicals other than PCBs, were generally unavailable for Lake Michigan. Only limited measurements of PCBs, toxaphene, and DDT in lower trophic levels could be found (Evans *et al*., 1991). These data are compared to model predictions in Figure 1.37. Bioaccumulation model predictions were scaled to match the concentrations reported for plankton; thus, the comparison is of relative accumulation above that trophic level. The model predicts PCBs accumulation very well. The model is not so successful in predicting accumulation of toxaphene, which is underpredicted in fish, and of DDT, where all trophic levels are underpredicted. The quality and representativeness of these data are questionable, however, because sample sizes were apparently small and variability in concentration measurements were not reported.

The most useful available data set for validating toxic chemical bioaccumulation simulations in the Great Lakes was developed for Lake Ontario (Oliver and Niimi, 1988; Oliver *et al*., 1989). These data included concentrations of PCBs and other HOCs in water, sediment, and biota, including all trophic levels. When normalized for the difference in exposure (water and sediment) concentrations between the two lakes, these data can be used to validate the MICHTOX steady-state bioaccumulation predictions. The MICHTOX predictions of lake trout bioaccumulation, expressed as bioaccumulation factors (BAF = $v/(c_d)$) for each toxic chemical are plotted with the Lake Ontario data in Figure 1.38. The predicted BAF for each toxic chemical is also tabulated in Table 1.8. Bioaccumulation factors are plotted as a function of log $K_{ow,}$ the chemical-specific parameter used to define toxicokinetic parameters in the model. The predicted trout bioaccumulation factors increase with log K_{ow} in agreement with the Lake Ontario data. The three toxic chemicals which diverge from this pattern, TCDF, BaP, and TCDD, are those which metabolize in fish. Although no data could be found to verify the BaP bioaccumulation simulation, the predictions for TCDF and TCDD can be verified. This requires that biota concentrations be normalized to those in sediment instead of water, because water concentration data for PCDFs and PCDDs are not available. This normalization is the biota-to-sediment ratio (BSR = $v/(r_S)$). BSR data and predictions are plotted as a function of log K_{ow} in Figure 1.39; PCDD/PCDF data are from Carey *et al*. (1990) and DeVault *et al*. (1989). The distinctly lower accumulation of PCDFs and PCDDs apparent in the Lake Ontario data is reflected in the BSR predictions for TCDF and TCDD.

1.6 Steady-State Model Applications

The steady-state model was used for four applications which explore different aspects of MICHTOX. First was to predict the concentrations expected in response to a unit load of each critical pollutant to the lake. Second, the steady-state model was used to quantify the magnitude of fate and transport fluxes of each toxic chemical in the mass balance model. This serves as a starting point

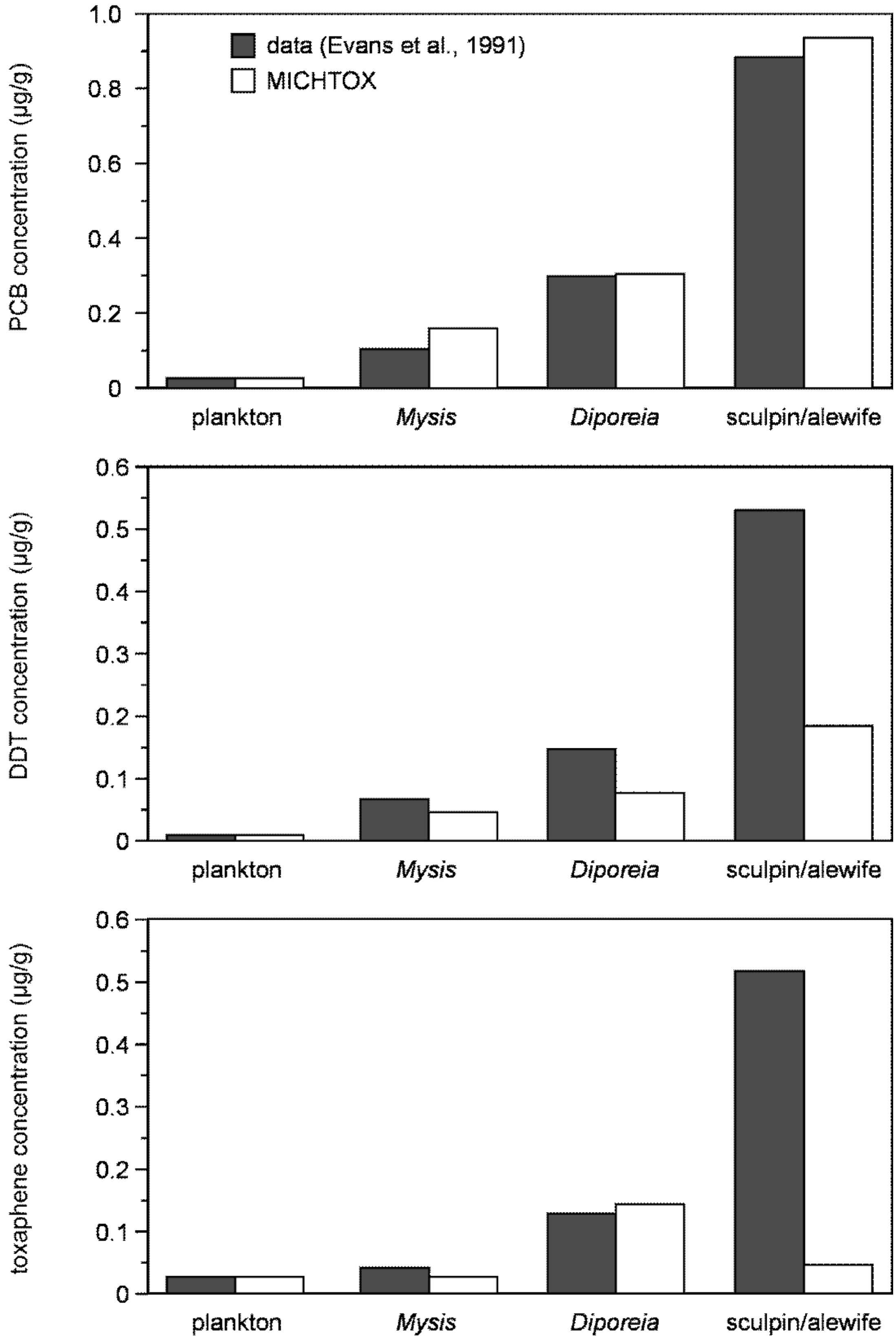


Figure 1.37. Validation of bioaccumulation predictions for lower trophic levels in Lake Michigan.

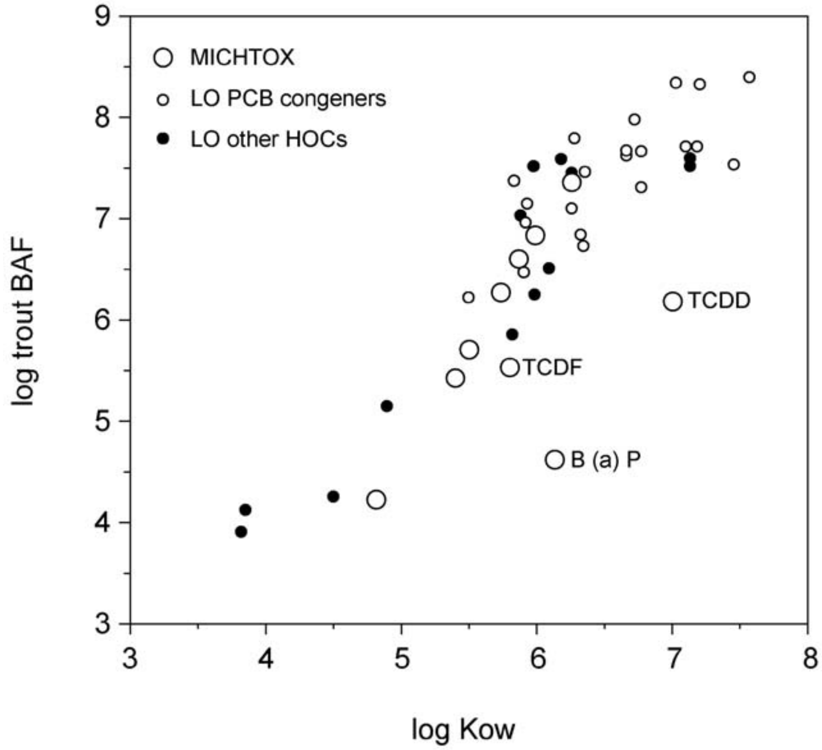


Figure 1.38. MICHTOX predicted trout bioaccumulation and data from Lake Ontario.

Table 1.8. Predicted Steady-State Bioaccumulation Factors (BAFs) for Critical Pollutants in Lake Michigan Lake Trout

Chemical	log BAF
PCB5	7.4
PCBs	7.0
Chlordane	6.8
DDT	6.8
PCB4	6.6
HCB	6.3
TCDD	6.2
Dieldrin	5.7
TCDF	5.5
Heptachlor epoxide	5.4
BaP	4.6
Toxaphene	4.2

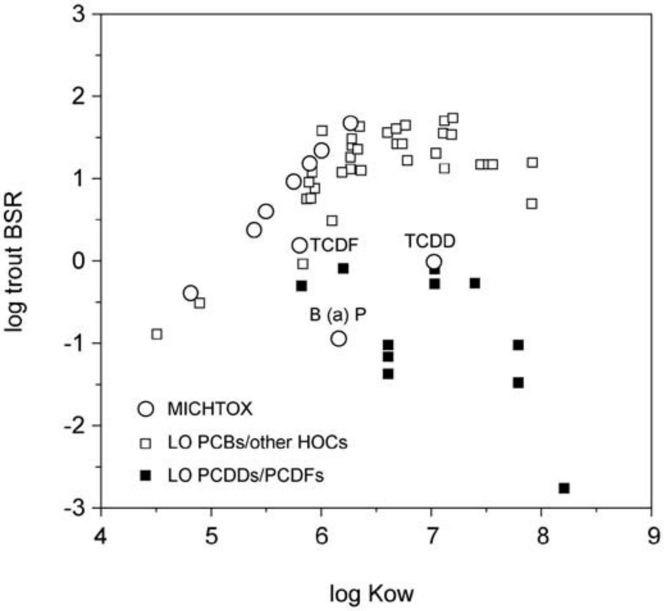


Figure 1.39. MICHTOX predicted trout biota-to-sediment ratio and data from Lake Ontario.

towards understanding differences in the mass balance results between chemicals, which can be quite large. The third application was sensitivity analysis, which displays the effect of varying individual model parameters upon predictions. Finally, the steady-state model was used as the principal vehicle for uncertainty analysis. Uncertainty analysis provides quantitative estimates of the uncertainty of model predictions.

Steady-state spreadsheet model output for each toxic chemical is attached as an appendix to this report. The spreadsheets document model input parameters, intermediate computations, results in terms of chemical concentrations in water and sediment in each model segment, and biota concentrations in southern Lake Michigan.

1.6.1 Steady-State Load-Response Predictions

Steady-state is the condition where concentration change (dc/dt) in response to a constant loading becomes negligibly small. Predicted steady-state concentrations of each toxic chemical in water, sediment, and lake trout are tabulated in Table 1.9. These are chemical concentrations predicted for southern Lake Michigan for a total unit loading to that segment of 1 kg/d. At steady-state, the model predicts a linear relationship between total loading and concentration. Thus, the results for a loading of 1 kg/d may be proportioned to any other load. This can be represented as a load-concentration diagram; the relationship for PCBs in water, for example, is plotted in Figure 1.40.

1.6.2 Mass Fate and Transport

The mass balance model works by computing the flux of chemical lost from the system (fate) and the fluxes transported between model segments. In the steady-state model, the total chemical load must be balanced by the losses and net transport. Therefore, the magnitude of all mass fluxes in a segment or segments of the model may be expressed as fractions of total load. This allows convenient comparison of the magnitude of chemical fluxes for different processes and for different chemicals. Such a comparison of steady-state mass fluxes for toxic chemicals in southern Lake Michigan is presented in Table 1.10. These fluxes were taken from model simulations made with expected air concentrations (Table 1.3) and, for PCBs, 1990 tributary loadings as well. The largest mass fluxes are internal cycling associated with particles (settling and resuspension) and particle burial, volatilization (absorption was included in the load), and, for BaP, photolysis. The other transport fluxes – advective transport, dispersive exchange, and sediment-water diffusion – are, in comparison, small to negligible. The mass balance processes identified as having the largest mass fluxes for a chemical also generally control the model predictions.

The magnitudes of fate and transport fluxes vary between chemicals, as shown in Table 1.10. They also vary significantly between different model segments. In Table 1.11, fate and transport fluxes for PCBs are presented for southern Lake Michigan and central Green Bay. The particle-associated fluxes of settling and resuspension, relative to segment loading, are much greater in central Green Bay. Transport, exchange, and volatilization fluxes are all larger in central Green Bay, whereas the burial flux is greater in southern Lake Michigan. In general, more fate and transport fluxes "participate" in the mass balance for the shallower Green Bay segments. This can be seen in Figure 1.41, which

Table 1.9. Predicted Steady-State Concentrations of Critical Pollutants in Lake Michigan for Unit Loading

Chemical	Water (pg/L)	Sediment (ng/g)	Trout (ng/g)
BaP	56	14	1.6
Chlordane	140	31	680
Dieldrin	440	51	190
DDT	150	32	700
HCB	60	9.6	89
Heptachlor epoxide	200	20	47
PCB4	84	16	240
PCB5	86	26	1200
PCBs	85	21	770
TCDD	87	44	41
TCDF	250	43	67
Toxaphene	940	39	15

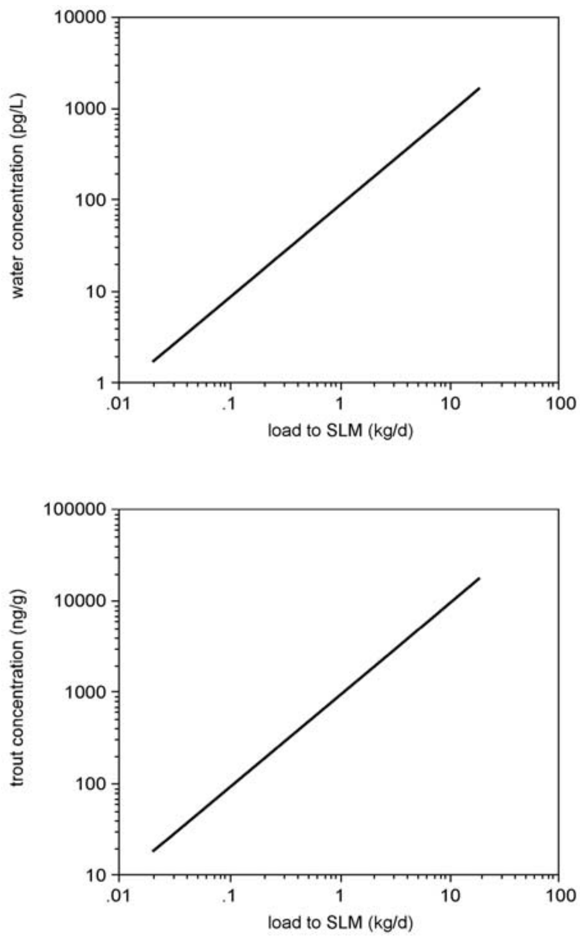


Figure 1.40. Load-concentration relationship for PCBs in southern Lake Michigan.

Table 1.10. Summary of Mass Fate and Transport for Critical Pollutants in Lake Michigan. Southern Lake Michigan Mass Fluxes Expressed as Fractions of Segment Load

Chemical	Volatilization	Photolysis	Transport	Exchange	Settling	Resuspension	Diffusion	Burial
BaP	1.9e-3	0.72	2.7e-3	4.8e-4	0.52	0.22	0.017	0.28
Chlordane	0.39	0	7.0e-3	6.0e-3	1.1	0.49	0.037	0.60
DDT	0.20	0.18	7.2e-3	6.1e-3	1.2	0.50	0.038	0.62
Dieldrin	0.038	3.5e-3	0.022	0.037	1.8	0.79	0.064	0.97
Heptachlor epoxide	0.61	0	9.8e-3	5.8e-3	0.72	0.31	0.026	0.38
HCB	0.81	2.2e-3	2.9e-3	5.9e-4	0.35	0.15	0.012	0.19
PCB4	0.68	0	4.1e-3	1.9e-3	0.58	0.25	0.019	0.31
PCB5	0.50	0	4.2e-3	1.1e-4	0.92	0.40	0.029	0.49
TCDD	0.042	0.11	4.2e-3	5.5e-3	1.6	0.68	0.049	0.85
TCDF	0.17	0	0.012	0.016	1.6	0.67	0.052	0.83
Toxaphene	0.24	0	0.046	0.037	1.4	0.60	0.063	0.75

Table 1.11. Comparison of PCBs Mass Fate and Transport for Critical Pollutants in Southern Lake Michigan and Central Green Bay

Segment	Volatilization	Transport	Exchange	Settling	Resuspension	Diffusion	Burial
Southern Lake Michigan	0.59	4.2e-3	1.0e-3	0.75	0.32	0.024	0.40
Central Green Bay	1.9	0.31	0.76	4.3	4.1	0.056	0.14

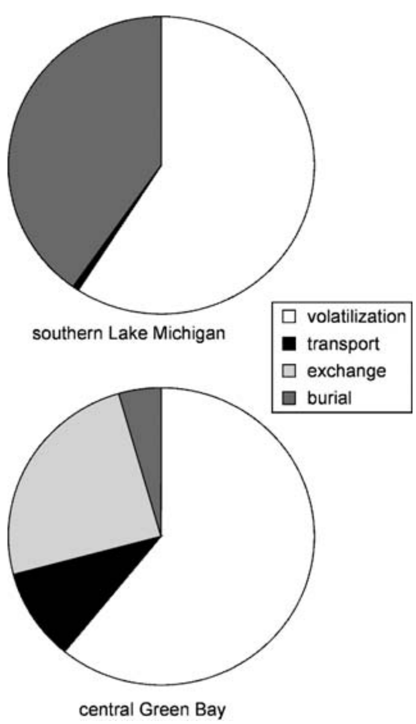


Figure 1.41. Relative magnitude of PCBs fate and transport fluxes.

portrays the relative magnitude of fate and transport fluxes for PCBs in southern Lake Michigan and central Green Bay. Settling and resuspension, which are internal cycling fluxes, have been removed from this figure.

A factor which can lead to confusion in interpreting model results (whether steady-state or dynamic) is the treatment of absorption. The confusion arises because absorption can be either treated as a component of net volatilization (a flux) or as a part of the atmospheric load. The motivation for the latter approach is that the three air-to-water chemical fluxes (wet and dry deposition and absorption) are all modeled as proportional to air concentration, which must be specified externally to this model. If the three are lumped together, then the resulting "total atmospheric load" is proportional to air concentration, and all other fluxes are proportional to water concentrations computed "inside" the model. If absorption is excluded from the atmospheric load, then atmospheric load will have an apparent greater effect upon predicted concentrations than other load components. Whether or not absorption is properly treated as a load or a boundary flux is academic; however, it is important to understand the distinction between atmospheric deposition and total atmospheric load. The significance of this distinction is displayed in Figure 1.42 for PCBs in southern Lake Michigan. Absorption is seen to be the largest air-to-water flux of PCBs, although the net volatilization flux is comparatively small.

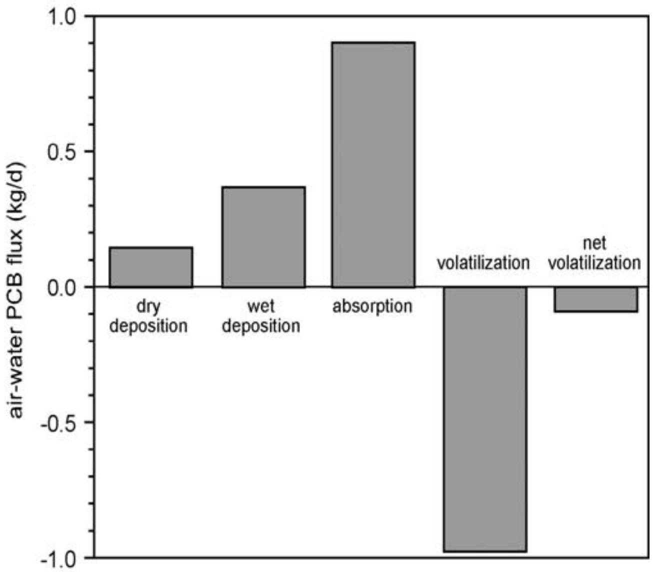


Figure 1.42. PCBs air-water fluxes at steady-state in southern Lake Michigan.

1.6.3 Sensitivity Analysis

Sensitivity analysis is a general method for model calibration; here it is used to demonstrate how MICHTOX is sensitive to individual chemical- and system-specific model parameters using PCBs as an example. The model was run repeatedly with a range of values for the parameter of interest. The change observed in model predictions provides an indication of model sensitivity to that particular parameter. Results of sensitivity analysis for PCBs are presented graphically in Figures 1.43 through 1.58. In most cases, parameter values were varied from one-tenth to ten times the estimated value, which generated the expected ("base case") prediction. Parameter values were varied simultaneously in all model segments; results are shown for southern Lake Michigan and central Green Bay segments.

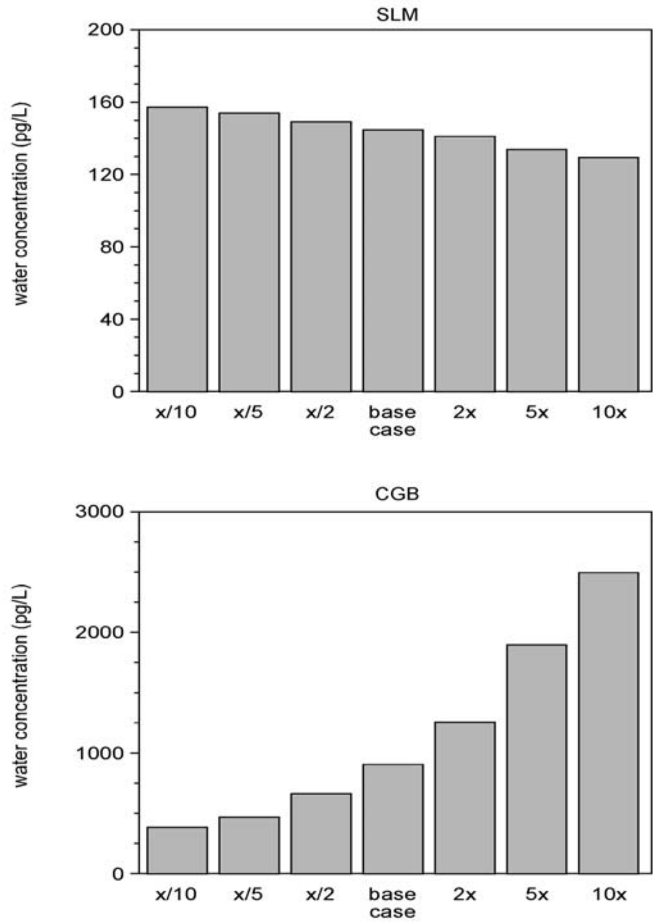


Figure 1.43. Sensitivity of water concentrations to K_{ow}.

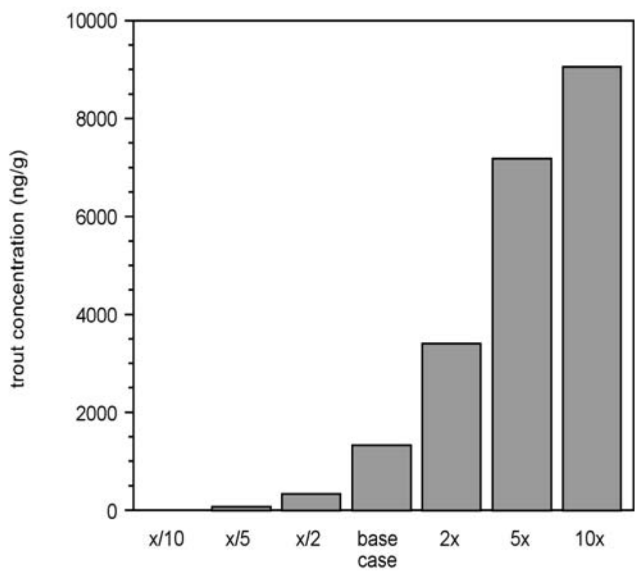


Figure 1.44. Sensitivity of trout concentrations to K_{ow}.

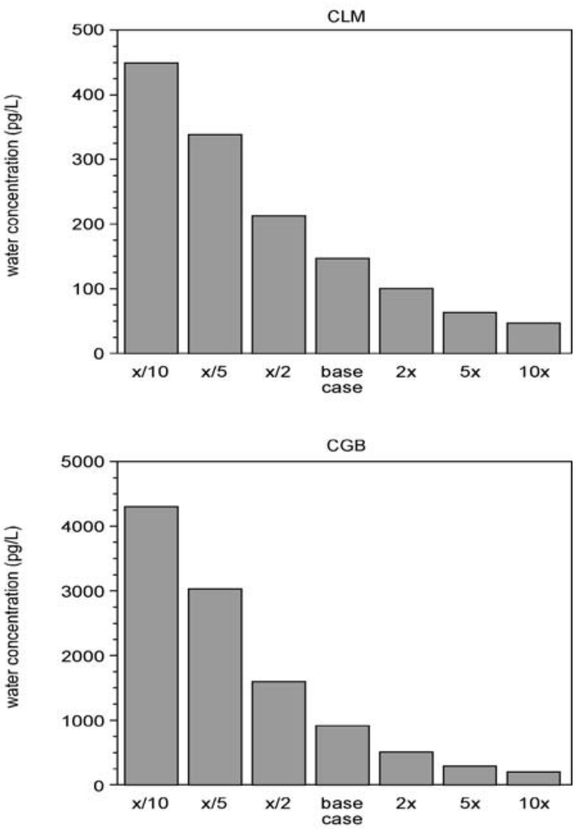


Figure 1.45. Sensitivity to Henry's constant.

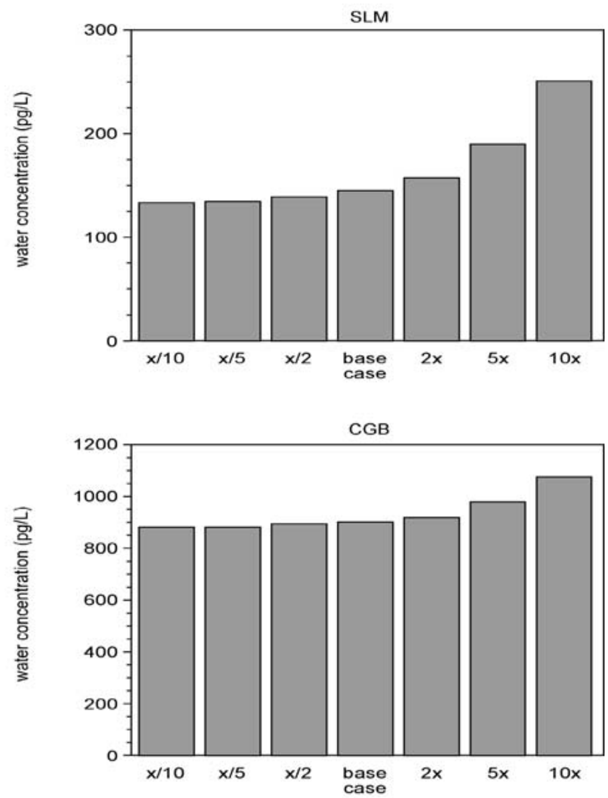


Figure 1.47. Sensitivity to dry deposition velocity.

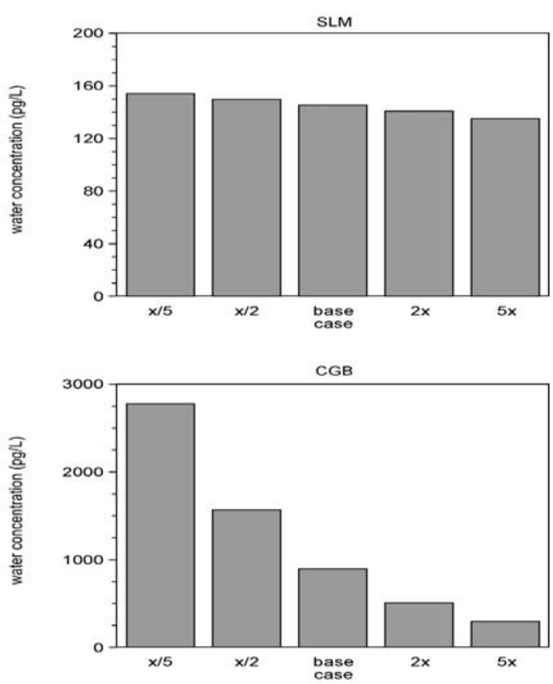


Figure 1.46. Sensitivity to volatilization rate.

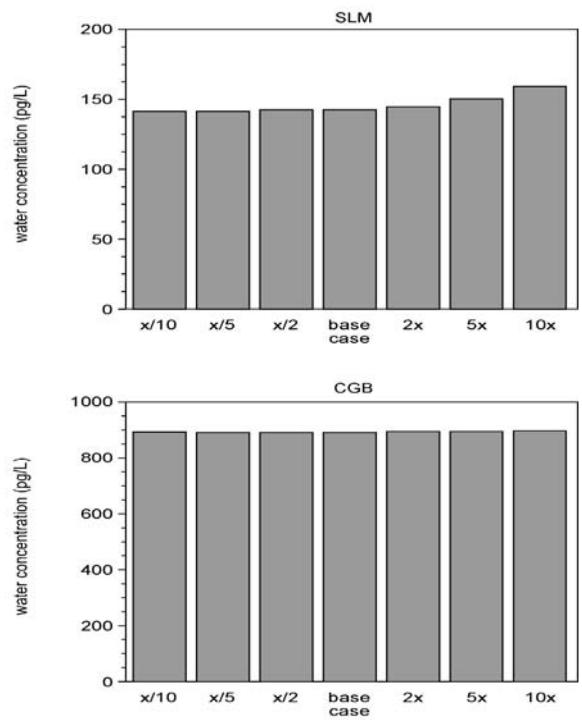


Figure 1.48. Sensitivity to sediment-water diffusion coefficient.

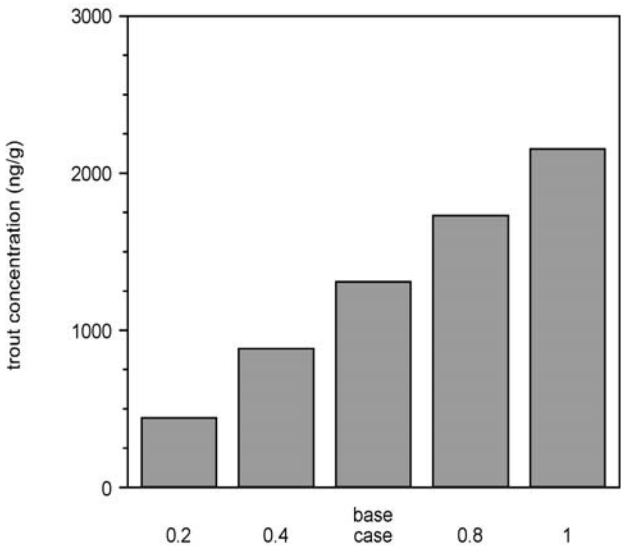


Figure 1.49. Sensitivity of trout concentration to chemical assimilation efficiency.

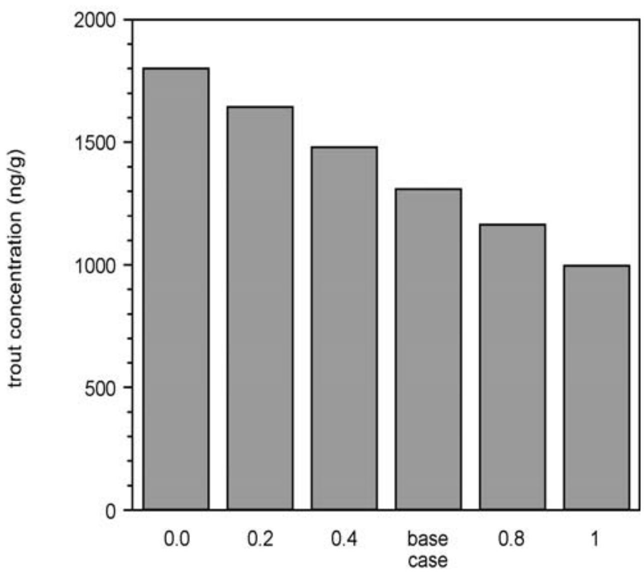


Figure 1.50. Sensitivity of trout concentration to pelagic diet fraction of forage fish.

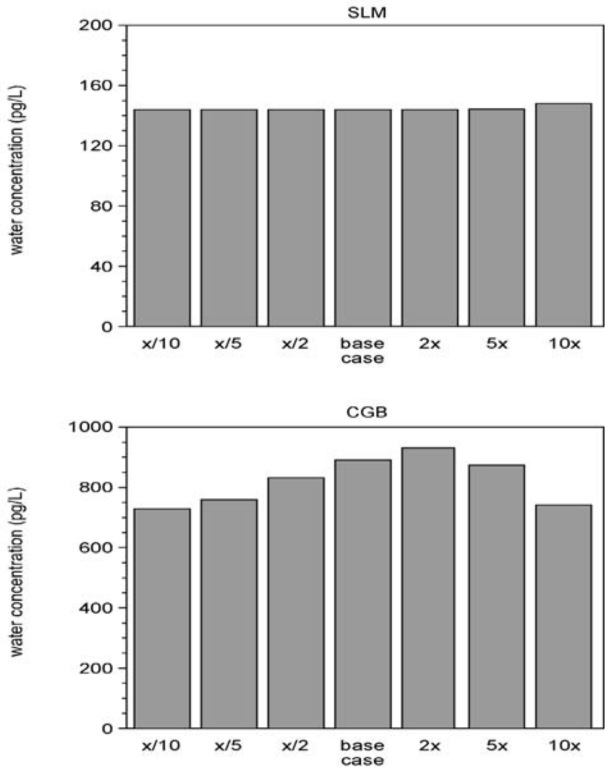


Figure 1.51. Sensitivity to dispersive exchange coefficient.

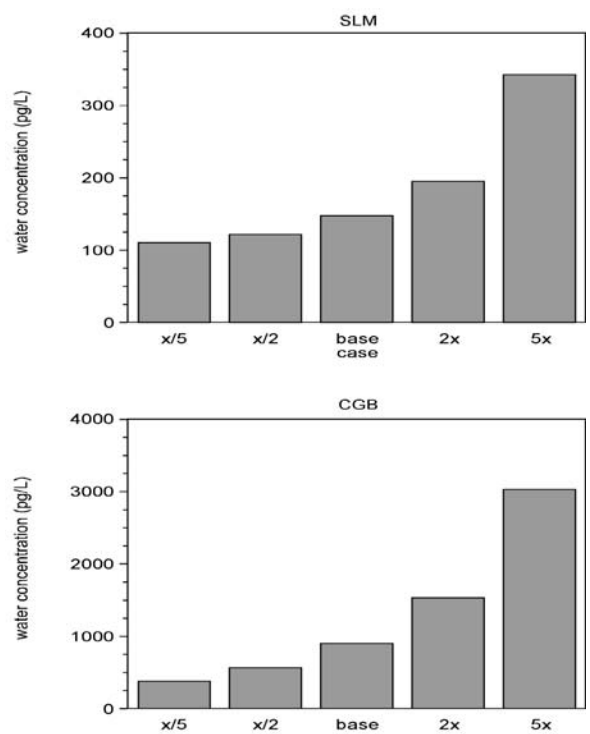


Figure 1.52 Sensitivity to suspended particle concentration.

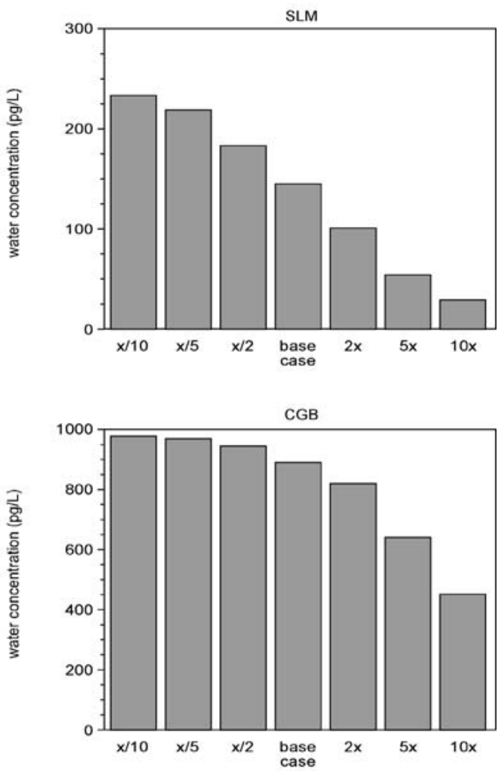


Figure 1.53. Sensitivity to particle burial velocity.

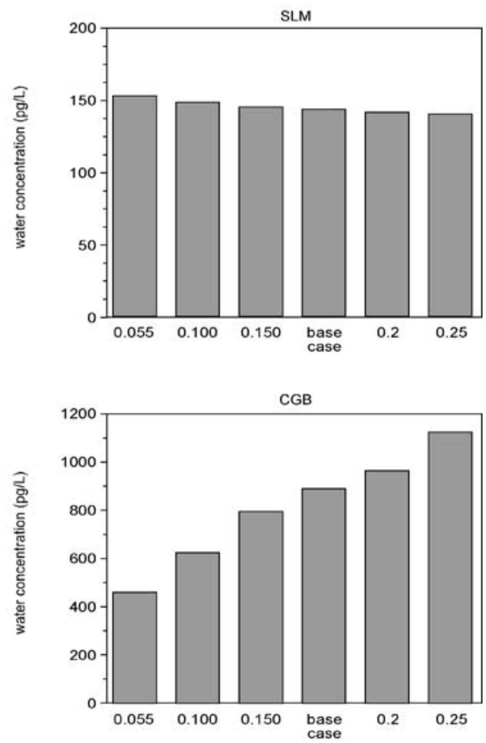


Figure 1.55. Sensitivity of water concentrations to suspended particle f_{oc}.

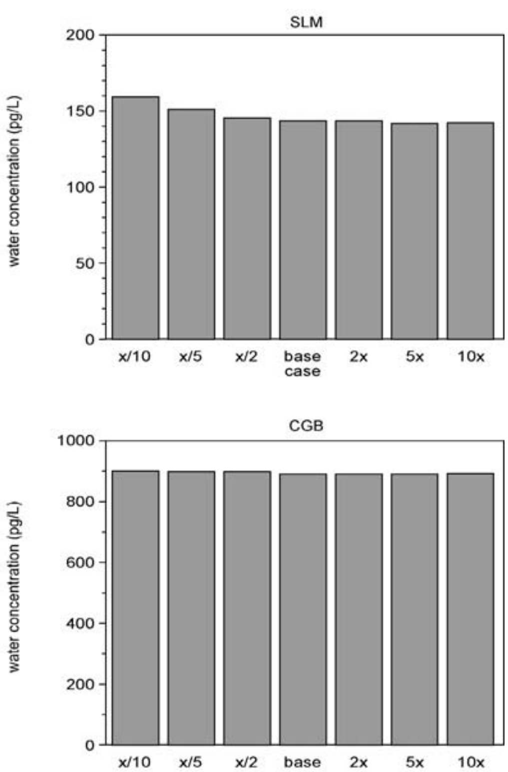


Figure 1.54. Sensitivity to particle settling velocity.

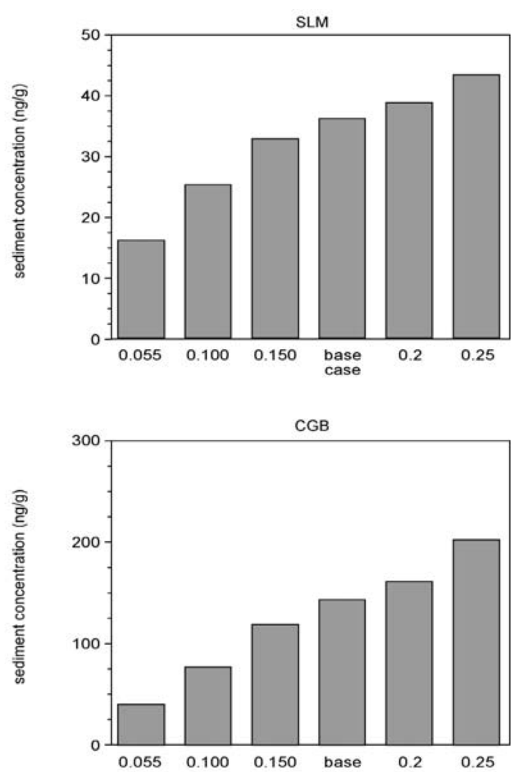


Figure 1.56. Sensitivity of sediment concentrations to suspended particle f_{oc}.

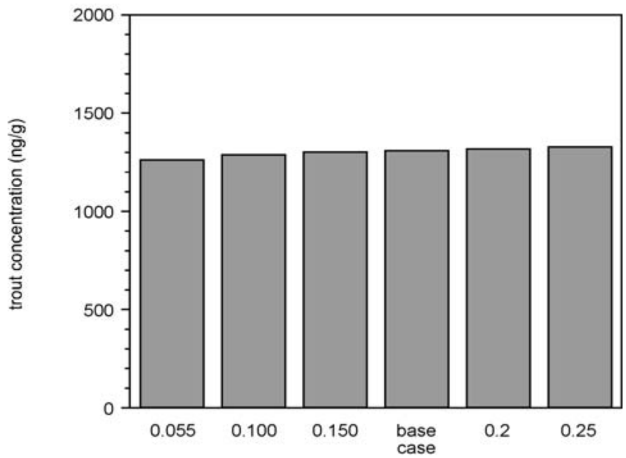


Figure 1.57. Sensitivity of trout concentrations to suspended particle f_{oc}.

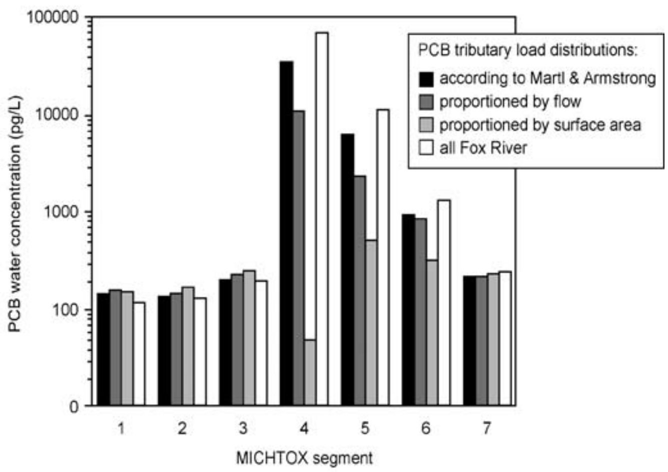


Figure 1.58. MICHTOX steady-state response to different tributary load distributions.

Sensitivity to chemical-specific parameters will be considered first. Figures 1.43 and 1.44 display the sensitivity of water and trout concentration predictions to K_{ow}. For water concentrations (Figure 1.43), sensitivity to K_{ow} is dramatically different in southern Lake Michigan and central Green Bay segments. In southern Lake Michigan, concentrations decline with increasing K_{ow} because chemical loss *via* sediment burial increases with partitioning, itself related to hydrophobicity. In central Green Bay, an opposite and much more dramatic, trend in sensitivity is observed. Increasing hydrophobicity again increases the extent of partitioning; however, concentrations increase because the predominant effect upon the mass balance is to reduce the volatilization flux. Figure 1.44 displays trout concentration sensitivity to K_{ow}. Here, the trend of concentration increasing with hydrophobicity – opposite that for the water in southern Lake Michigan – is observed, and the predictions are very sensitive to K_{ow}. Trout concentrations decline by a factor of 140 as K_{ow} is reduced by a factor of 10, while concentrations increase by seven times as K_{ow} increases by a factor of 10.

Sensitivity to Henry's constant is shown in Figure 1.45. A significant decline in water concentration is predicted as Henry's constant increases, because volatility, and hence, volatilization loss increases with Henry's constant. Model sensitivity to volatilization rate is shown in Figure 1.46. The sensitivity to volatilization rate is much greater in central Green Bay because the air-water flux gradient is substantially greater there than it is in southern Lake Michigan. Figure 1.47 displays the model sensitivity to dry deposition velocity, the parameter which defines the dry deposition flux from the atmosphere. The model is sensitive to dry deposition velocity only for parameter values greater than the expected value, as is expected for a parameter related to chemical loading. The model is minimally sensitive to the sediment-water diffusive exchange coefficient, Figure 1.48, in southern Lake Michigan, and particularly in central Green Bay.

Two additional parameters of the bioaccumulation model were evaluated by sensitivity analysis. Trout concentration predictions vary proportionately with chemical assimilation efficiency in trout (Figure 1.49) because essentially all PCBs accumulation occurs from food consumption. Model sensitivity to the pelagic diet fraction of alewife is shown in Figure 1.50. (A pelagic diet fraction of zero means alewife consume benthos exclusively.) Trout concentrations decline with increasing pelagic diet fraction, indicating that a shift to benthic feeding is expected to result in greater chemical accumulation in higher trophic levels. This reflects the fact that, for water and sediment concentrations at steady-state, *Diporeia* is a more contaminated food item than *Mysis*.

Sensitivity of model predictions to circulation transport was evaluated by varying the dispersive exchange coefficient. Figure 1.51 displays the sensitivity to this parameter. In southern Lake Michigan, the coefficients must be increased ten-fold to observe any response, reflecting both the relative insignificance of horizontal exchange here and the lack of a chemical gradient between the main lake segments. In central Green Bay, the model is more sensitive to horizontal exchange, the concentration gradients are greater, and the circulation is a more significant mass balance process. Concentrations in central Green Bay decrease for exchange coefficients both lesser and greater than the expected values, a sensitivity more complex than observed for other model parameters. At low exchange values, the flux of PCBs to central Green Bay from the Fox River and inner Green Bay is retarded, which lowers central Green Bay concentrations. At high values of exchange, PCBs in Green Bay are substantially diluted by main lake water, again lowering central Green Bay concentrations.

Model sensitivity to several particle-related parameters was also tested. Sensitivity to suspended particle concentration (M) is plotted in Figure 1.52. Water concentrations increase with M because of the shift in particle-sorbed chemical from the sediment to the water column. The dissolved chemical fraction is also lowered and, hence, volatilization. Sensitivity of trout concentrations to M (not plotted) is virtually negligible. The increase in water concentration with M is offset by the decline in the dissolved chemical fraction, so that the chemical exposure to biota is relatively unaffected. Figure 1.53 displays the model sensitivity to particle burial velocity; increasing the burial velocity reduces the water concentration. Because burial is a predominant loss process for PCBs in southern Lake Michigan, sensitivity to burial velocity is observed across the range of parameters. In central Green Bay, however, sensitivity is only observed for high burial velocities. Sensitivity to particle settling velocity is plotted in Figure 1.54. As settling velocity increases, the solids balance requires resuspension to increase as well. Thus, the intensity of particle mixing between water and sediment grows with increasing settling velocity. Because particulate chemical concentrations (r) are nearly equal in the water and sediment at steady-state, the model's sensitivity to this parameter is minimal.

The sensitivity of model predictions to suspended particle organic carbon was also evaluated because it is the organic carbon fraction of particles which actively sorbs HOCs. The model sensitivity to f_{oc} is somewhat different than that to M because organic carbon is not constrained by a mass balance in this model. The development of a carbon-based particle balance was a principal goal of the modeling effort for the GBMBP. Sensitivity of water concentrations to f_{oc} is displayed in Figure 1.55, indicating different responses in southern Lake Michigan and central Green Bay. In southern Lake Michigan water, concentrations decline slightly with increasing f_{oc}, as the flux of chemical settling to the sediment increases. In central Green Bay, there is a much greater increase in concentration with f_{oc}, which lowers dissolved chemical fractions and volatilization loss. In the sediment (Figure 1.56), however, both segments show an increasing concentration with f_{oc}. Figure 1.57 sensitivity of trout concentrations to f_{oc}; as was the case for M, biota concentrations are fairly insensitive to this parameter.

One additional factor, the spatial distribution of tributary loading, was evaluated for model sensitivity. Loading distribution may be expected to affect the distribution of chemical concentrations throughout the system. Thus sensitivity in each model segment was evaluated. Several possible loading distributions were considered, although the total PCBs tributary loading to the lake, 1 kg/d, was not varied. These included the distribution based upon Marti and Armstrong's (1990) tributary sampling, distributions based upon tributary flow to each segment and segment surface area, and distributions based on allocating all loading to the Fox River. The results appear in Figure 1.58. Although water column concentrations are plotted, sediment concentration distributions were similar. Concentrations in the main lake segments (1, 2, and 3) are relatively insensitive to load distribution and show little spatial gradient. Because of their large surface areas, these segments receive much of their PCBs load from the atmosphere. Thus their insensitivity to tributary load distribution is not unexpected. In Green Bay segments (5, 6, and 7), both sensitivities to tributary load distribution and the spatial concentration gradients are much more pronounced.

Concentrations are sensitive to the distribution of tributary (or other spatially variable) loading in these segments primarily because tributary load makes up most of the total chemical loading to Green Bay and because horizontal transport and exchange are more important processes in these relatively isolated segments. The "all Fox River" case demonstrates the predicted effect of PCBs loading from that tributary to the entire lake. Much of PCBs mass from that source has been lost (principally by volatilization) before it reaches the main lake. Of the 1 kg/d loading to the Fox River, only 31 g/d are predicted to reach the main lake.

A number of general observations about model behavior may be drawn from the sensitivity analysis. The first is that sensitivity to parameters do not vary uniformly throughout the model's segments and state variables. Rather, the magnitude and even the direction of changes in concentration vary according to segment and state variable. The observed sensitivities are strongly related to the relative magnitude of the various chemical fluxes in a particular model segment. Parameter sensitivity is often not uniform across a range of parameter values. Finally, biota concentrations are largely sensitive to bioaccumulation model parameters but are less sensitive to parameters of the mass balance model.

1.6.4 Uncertainty Analysis

Model predictions may be erroneous for a number of reasons, including parameterization errors, conceptual and descriptive errors, and algorithm errors (bugs). Calibration and verification procedures are usually relied upon to detect and correct such errors in water quality models. Because extensive calibration/verification of this model was not possible, the possibility of undetected errors makes MICHTOX predictions uncertain. Uncertainty analysis was used to address and quantify uncertainty in model predictions, particularly relating to parameterization errors. Conceptual and descriptive errors in the model were neglected because these factors relate to possibilities which would change model results to an unforeseeable extent. Uncertainty due to these errors can only be identified by more comprehensive model calibration and verification. Modeling quality assurance, hopefully, prevented major mishaps due to bugs.

For the most part, uncertainty analysis was performed on the steady-state model. This was a choice constrained by the 8000 model runs necessary to perform the analysis. A more limited analysis of the dynamic model was performed; this is described in a later section of the report.

1.6.4.1 Analysis of Model Uncertainty

Uncertainty analysis was performed by the Monte Carlo method. This method allows direct analysis of the consequence of model parameter uncertainty because the model is used to compute changes in concentration resulting from changes in parameter values. This is achieved by performing repeated simulations of the model with randomly selected values from defined probability distributions. For each simulation, parameter values are defined as random variables whose distribution is a measure of uncertainty in the real but unknown value of the parameter. In this application, parameter variability was assumed to be uncorrelated, and parameter values were chosen at random from specified (exact) frequency distributions. This is known as the Latin Hypercube method (McKay *et al*., 1979). The process is repeated for a number of iterations sufficient to converge upon an estimate of the frequency distribution of the output variables. Monte Carlo analysis allows a probabilistic statement of uncertainty to be made because a distribution of model predictions are produced (Gardner and O'Neill, 1983). Details of the implementation of uncertainty analysis for toxic chemical models is provided in Endicott *et al*. (1990, 1991). Parameter distributions were formed from data available in the literature and from experience gained in calibrating other models. Probability distributions for model parameters treated as uncertain are tabulated in Table 1.12. Because many of these parameters had expected values that varied between model segments or trophic levels, scale factors were used to simultaneously vary the parameter values. For example, flows between water column segments were varied by multiplying the expected value of each flow by the scale factor, the probability distribution of which is found in the table. In this way, parameter variability in each segment and trophic level was generated, and random selection of every parameter value was avoided. This reduced the number of parameter selections per iteration from 80 to 31.

Table 1.12. Probability Distribution for Steady-State Model Uncertainty Analysis

Group	Parameter	Type*	Distribution	Mean	CV	95% CI	
Lake circulation	Flow	SF	LN		0.10		
	Dispersive exchange	SF	LN		0.10		
	Pore water diffusive exchange	PV	LN	3.0e-4	0.64	1.0e-4	1.0e-3
Particle transport	Settling velocity	SF	N		0.11		
	Burial velocity	SF	LN		0.18		
	Suspended particle concentrations	SF	LN		0.35		
Organic carbon	Suspended particle f_{oc}	SF	LN		0.25		
	Water column colloidal binding efficiency	PV	LU			0.50	1.0
	Sediment particle f_{oc}	PV	N		0.24	0.0017	0.047
	Pore water dissolved organic carbon binding efficiency	PV	N	0.050	0.25	0.34	1.0
	Log K_{oc} error	RE	N	0.67	0.30		
Atmospheric	Aerosol volumetric fraction	PV	LN		0.046	6.3e-12	6.3e-11
	Particle scavenging ratio	PV	N	2.0e-11	0.37	55,000	350,000
	Dry deposition velocity	PV	LN	200,000	0.43	86	430
				190			
Bioaccumulation	Dissolved oxygen concentration	PV	N		0.10	8.0	12.0
	Alewife pelagic diet fraction	PV	N	10	0.11	0.50	0.80
	Lipid content	SF	N	0.062	0.11		
	Benthic log chemical assimilation efficiency error	RE	N		0.26		
	Lake trout chemical assimilation efficiency	PV	N		0.085	0.50	0.70
	Food assimilation efficiency	SF	N	0.06	0.064		
	Growth rate	SF	LN		0.18		
	Respiration rate	SF	LN		0.18		
	Chemical metabolism: BaP	PV	LN		0.64	0.0072	0.072
	TCDD/TCDF	PV	N	0.023	0.36	0.0010	0.0060
	Chemical uptake efficiency error	RE	N	0.0035	0.051		

*SF: scale factor; PV: parameter value; RE: regression error; N: normal distribution; LN: lognormal distribution; LU: loguniform distribution.

1.6.4.2 Results

Three different tests of predictive uncertainty were performed on the steady-state model. The first test performed for each toxic chemical evaluated predictive uncertainty due solely to uncertain parameters with a fixed air concentration of 1 ng/m^3. The second test treated air concentration as uncertain, and was again performed for each chemical. This represented the more realistic condition where loadings as well as model parameters are uncertain. The third test, performed on PCBs, included a constant tributary load to simulations in which air concentration and model parameters were both treated as uncertain. This test was repeated over a range of tributary loads; it displays the predicted response (with uncertainty) to partial control of loadings.

The output probability distributions for 200 iterations were used to assure convergence in the uncertainty analysis. The model output distributions were approximately lognormal for all chemicals and all tests. The logarithmic means of the Monte Carlo output distributions agreed with predictions of the steady-state model made with expected (mean) values of all parameters. Thus, the results of the uncertainty analysis were consistent with the central limit theorem.

Results for the first test are summarized in Table 1.13, including logarithmic mean, logarithmic

Table 1.13. Summary of Results for First Test of Model Uncertainty. Predicted Steady-State Concentrations for Fixed Air Concentrations of 1 ng/m^3 for Each Chemical

	Water Concentration (pg/L)		95% CI		Lake Trout Concentration (ng/g)		95% CI	
Chemical	**Log Mean**	**lnCV**	**LCL***	**UCL****	**Log Mean**	**lnCV**	**LCL**	**UCL**
BaP	9940	0.46	410	2500	26	1.9	2.2	270
Chlordane	1200	0.40	560	2500	4900	1.8	330	3.5e+04
DDT	1900	0.43	870	4400	8000	1.3	910	4.9e+04
Dieldrin	7200	0.82	1900	31000	2700	2.8	140	4.8e+04
HCB	32	0.90	6.7	140	42	1.7	4.3	410
Heptachlor epoxide	1500	0.74	370	5000	340	2.5	20	5000
PCBs	450	0.66	130	1350	3200	1.0	550	1.6+04
TCDD	1600	0.44	730	3700	730	1.2	150	5600
TCDF	3900	0.55	1600	12000	1000	1.2	130	5000
Toxaphene	11000	4100	4100	31000	190	1.1	41	1300

*Lower confidence limits
**Upper confidence limits

coefficient of variation, and 95% confidence intervals of the distribution of model predictions for water and trout in southern Lake Michigan. The results of this test show that the uncertainty of water and, particularly, trout predictions are very large for each channel. The widths of the 95% confidence intervals for predicted water concentrations generally span a factor of 10; HCB, dieldrin, and heptachlor epoxide had greater uncertainty. For trout, confidence intervals span widths varying from factors of 30 (PCBs) to 300 (dieldrin). Trout concentration predictions are expected to be more uncertain than those for water because uncertainty in the bioaccumulation model amplifies the uncertainty generated in the mass balance model.

Although these uncertainties are large, they are fairly comparable to the variability reported for toxic chemical concentrations in aquatic ecosystems. For example, the coefficient of variance (CV) for predicted PCBs trout concentrations is 1.0; if these predictions are converted to bioaccumulation factors, then the variability is reduced to a CV of 0.76. In comparison, the CV calculated from 1971 Lake Michigan fish data (normalized for lipid) is about 0.75 (Connolly, 1992). Across a range of ecosystems and HOCs, significant variability in BAF is observed. For chemicals in the range $6 < \log K_{ow} < 7$, Connolly reports a bioaccumulation factor CV of 1.6. In this context, the uncertainty of model predictions appears more reasonable, and it reflects the magnitude of variability in the data.

The results in Table 1.13 may be used to define confidence limits for the steady-state load-concentration relationships because air concentrations may be converted to total chemical load. Such a result is displayed for PCBs in southern Lake Michigan in Figure 1.59. The results also predict the relative potential of each toxic chemical, for a given air concentration, to accumulate in Lake Michigan. Toxaphene has the greatest accumulation potential in water; HCB has the least. For trout, DDT, chlordane, PCBs, and dieldrin have the greatest accumulation potential; BaP has the least.

In the second test, air concentrations were treated as uncertain. Thus, greater predictive uncertainty was expected. Results of this test, presented in Table 1.14, show that uncertainties have grown from the previous test, particularly for those chemicals with largely uncertain air concentrations. This is most apparent for water concentration predictions with much larger CVs for chlordane, DDT, TCDD, TCDF, and, particularly, toxaphene. Uncertainty in trout concentration predictions were generally less affected by air concentration uncertainty, except for dieldrin and toxaphene. Apparently, the impact of uncertainty in air concentrations upon predictive

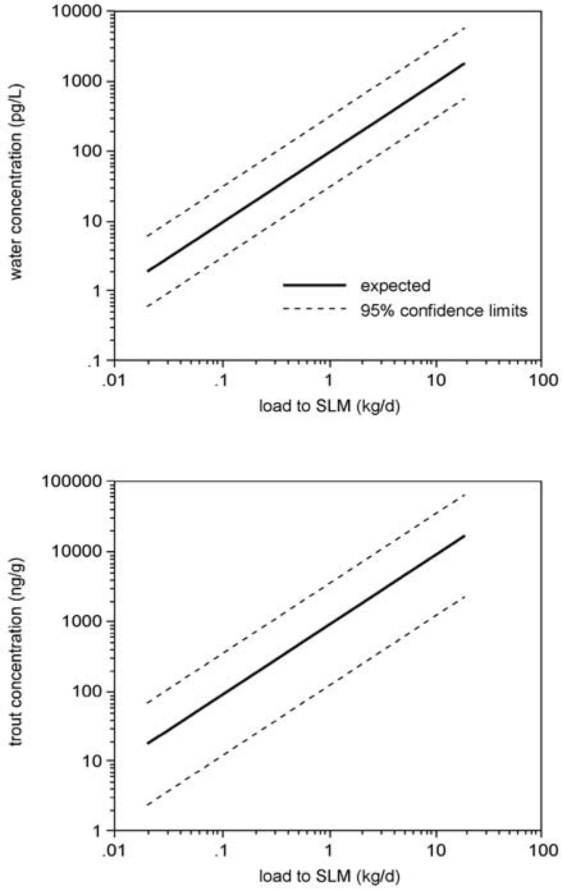


Figure 1.59. Load-concentration relationship for PCBs in southern Lake Michigan including confidence limits.

Table 1.14. Summary of Results for Second Test of Model Uncertainty. Predicted Steady-State Concentrations for Expected Air Concentrations of Each Chemical

	Water Concentration (pg/L)		95% CI		Lake Trout Concentration (ng/g)		95% CI	
Chemical	**Log Mean**	**lnCV**	**LCL**	**UCL**	**Log Mean**	**lnCV**	**LCL**	**UCL**
BaP	510	0.57	1.7	1400	0.13	2.0	99e-03	1.4
Chlordane	48	0.70	14	170	190	1.9	19	2300
DDT	57	0.74	16	210	240	1.4	26	1500
Dieldrin	240	1.00	48	1300	88	3.6	3.5	2000
HCB	1.4	1.1	0.22	7.1	1.9	1.7	0.19	17
Heptachlor epoxide	25	0.92	5.4	120	5.6	2.7	0.32	96
PCBs	110	0.64	33	330	780	1.0	150	4000
TCDD	0.049	0.77	0.012	0.18	0.023	1.3	3.7e-03	0.20
TCDF	1.3	0.83	190	5.1	0.34	1.4	0.039	2.5
Toxaphene	2000	1.7	190	1.8e+04	35	2.4	2.2	5010

uncertainty varies among chemicals, and the impact may be different in water and trout.

These results may also be considered to be predicted steady-state concentrations for the toxic chemicals, if the predominant continuing load is atmospheric. Conversely, the results may be used to test whether the estimated air concentrations for each chemical are consistent with observed concentrations in Lake Michigan. If observed chemical concentrations fall outside the 95% confidence limits of the predictions, then the estimated air concentrations used in the model are probably incorrect. Data used to evaluate the predictions were obtained from a variety of sources (Environment Canada, 1991; Michigan Department of Natural Resources, 1990; U.S. Environmental Protection Agency, 1989b; DeVault *et al*., 1986). Results of this test suggest that BaP, TCDD, and TCDF air concentrations are probably lower than their expected values, and air concentrations of HCB are probably higher. Observed concentrations of the other chemicals fall within the confidence limits of the predictions.

The third uncertainty analysis test was a modification of the second, with a constant tributary loading in addition to uncertain model parameters and air concentrations. This test, performed for PCBs only, was repeated over a range of tributary loadings from 0.02 to 2 kg/d. The spatial distribution of tributary loads was the same described for PCBs verification. Results of this test appear in Table 1.15. As tributary loading increases, the uncertainty in predicted concentrations declines. This is because the influence of air concentration uncertainty upon predictions diminishes as atmospheric deposition becomes a relatively smaller load component in comparison to the growing tributary load. In other words, increasing the tributary load reduces total load uncertainty, which was reflected in the uncertainty of predictions. The second insight offered by this test was that predicted concentrations do not respond proportionately with tributary loading, independently of air concentrations. This can be seen in Figures 1.60 (water) and 1.61 (trout) in which the results of this test appear as load-concentration plots. As tributary loading declines, so do water and trout concentrations – but only so far. The factor which limits the effectiveness of tributary loading reduction is the air concentration. Large reductions in tributary loading cannot be expected to produce similarly large improvements in water quality if atmospheric loading is not reduced as well. Because the estimated tributary loading of PCBs is currently about 1 kg/d, Lake Michigan is already in the situation where water quality improvement for this chemical must come largely from reductions in atmospheric loading.

1.6.4.3 Critical Parameterization Uncertainty

Given that uncertainties in model predictions are undesirably large, how can the situation be improved? The large predictive uncertainties may be "reigned in" by further calibration and verification of the model. This would require collection of additional monitoring data for toxic chemicals, emphasizing determination of chemical loads. Aside from estimating the confidence intervals for model predictions, uncertainty analysis can identify the "contribution" of model parameters to uncertainty in

Table 1.15. Summary of Results for Third Test of Model Uncertainty. Predicted Steady-State PCBs Concentrations for Varying Tributary Loads and Expected Air Concentration

	Water Concentration (pg/L)		95% CI		Lake Trout Concentration (ng/g)		95% CI	
Load (kg/d)l	Log Mean	lnCV	LCL	UCL	Log Mean	lnCV	LCL	UCL
0.02	110	0.63	34	330	780	0.99	160	4000
0.2	120	0.60	38	340	840	0.96	180	4200
2	190	0.46	81	450	1400	0.91	290	6000

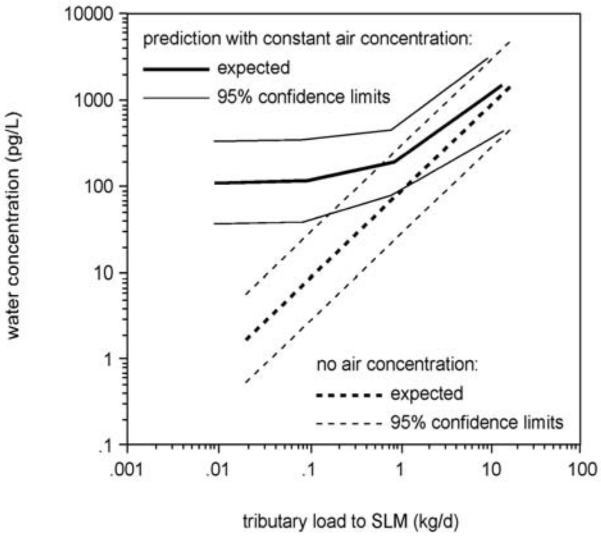


Figure 1.60. Load-concentration relationship for PCBs in southern Lake Michigan water: Effect of constant air concentration.

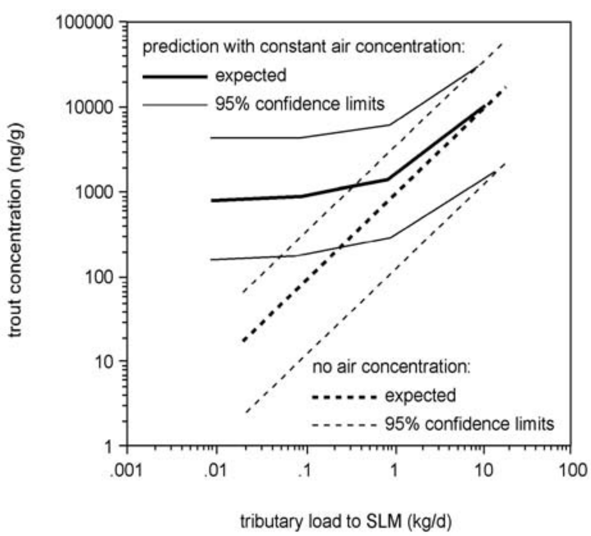


Figure 1.61. Load-concentration relationship for PCBs in southern Lake Michigan trout: Effect of constant air concentration.

The degree of correlation observed between parameter and prediction values in Monte Carlo testing indicates the relative importance of an uncertain parameter in contributing to prediction uncertainty. The square of the correlation coefficient, r^2, is an estimate of the fraction of prediction uncertainty attributable to each uncertain parameter. Correlation analysis was performed on the results of the second uncertainty analysis test (uncertain model parameters/uncertain air concentrations) for five of the toxic chemicals: BaP, chlordane, dieldrin, PCB5, and TCDD. Results are presented graphically in Figure 1.62 for water concentration predictions and in Figure 1.63 for trout predictions. For both water and trout, a relatively few critical parameters were identified which contribute most of the uncertainty in model predictions. The relative contribution of these parameters to predictive uncertainty was, however, fairly chemical-specific and related to the hydrophobicity and reactivity of each chemical. As expected, air concentrations contribute large uncertainties to water concentration predictions. Parameters related to air-water chemical flux – scavenging ratio, Henry's constant, and aerosol volume fraction – were also found to be significant contributors to predictive uncertainty. Other critical parameters for water prediction uncertainty include: suspended particle concentration, particle burial rate, and for BaP, photolysis rate. Significantly, several parameters were not identified as critical: advective and dispersive transport, air-water transfer coefficients, and organic carbon fractions. The predictions. Therefore, an alternative approach to reducing uncertainty would be to prioritize research efforts intended to improve the accuracy of model predictions by accurately measuring "critical" parameters identified as major contributors to predictive uncertainty. The optimum strategy for reducing predictive uncertainty would be a combination of the two approaches.

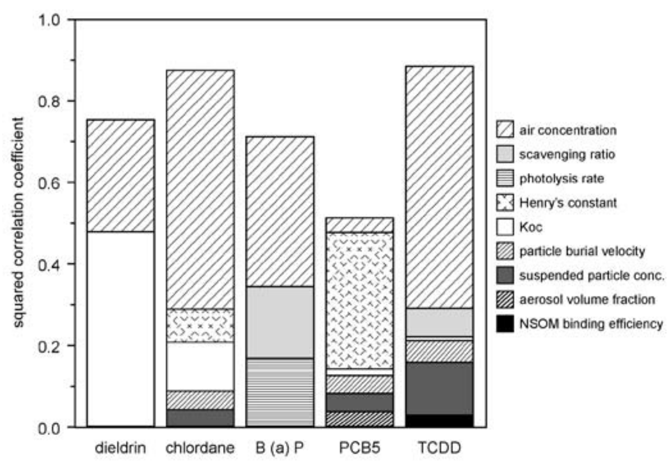


Figure 1.62. Contribution of critical parameters to steady-state model uncertainty: Water concentration.

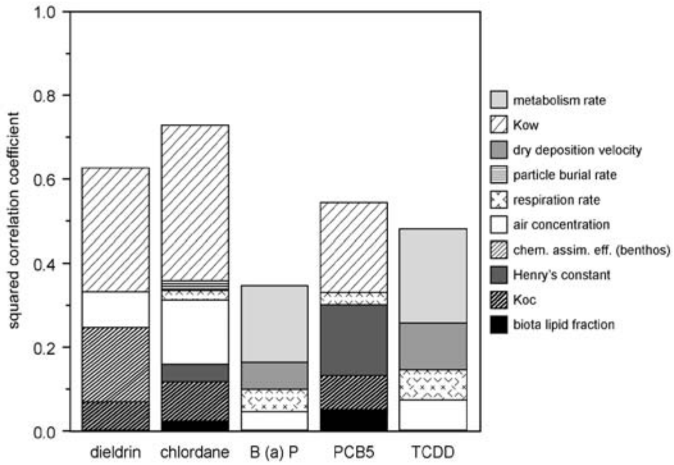


Figure 1.63. Contribution of critical parameters to steady-state model uncertainty: Trout concentration.

organic carbon partition coefficient, while critical for the less hydrophobic chemicals (dieldrin and chlordane), was not identified as critical for the more hydrophobic chemicals (BaP, PCB5, and TCDD).

Generally, the critical parameters are related to chemical sources (in this case, atmospheric input) and loss mechanisms (burial, photolysis).

For trout predictions, air concentrations are a lesser but still significant source of uncertainty, except for PCB5. Critical parameters for trout include K_{ow} (primarily by determining excretion rate) and other bioaccumulation parameters: metabolization (for BaP and TCDD), respiration, benthos chemical assimilation efficiency, and lipid fraction; burial rate, dry deposition velocity, Henry's constant, and K_{oc} are also critical. K_{oc} appears because it was used to calculate the plankton BCF. For BaP and TCDD, M_c is the most critical parameter; for the other chemicals, K_{ow} is most critical. It should be noted that these are parameters which, along with H_{lc}, could be made "certain" for selected chemicals by direct laboratory measurements. Greater than half of the uncertainty in trout predictions is contributed by parameters which define the chemical exposure. For trout, as well as water predictions, both chemical- and system-specific parameters were identified as critical.

The model uncertainties estimated by this analysis are surprisingly large. In comparison, the results of verification for plutonium, lead, and PCBs suggest much greater model certainty. These seemingly contradictory results may be reconciled by considering the differences between model verification and uncertainty analysis. Verification was performed on three chemicals for which model parameterization was fairly well-defined; i.e., there were reliable data from which to select expected parameter values. In addition, chemical loads and ambient concentrations were known (or estimated) for these chemicals in Lake Michigan. Finally, prior modeling efforts for each of these chemicals had been conducted, which assisted in developing this model. As a result, the qualitative agreement between predictions and data obtained in verification was expected. On the other hand, uncertainty analysis was performed on model simulations for 11 chemicals of which the majority have not been measured throughout the Lake Michigan ecosystem or for which model parameters and forcing functions have never been determined. To perform such simulations requires that model parameters be extrapolated from physicochemical properties, such as K_{ow}, H_{lc}, and M_c, which are themselves uncertain. As a result, confidence in the parameterization is reduced, translating into large predictive uncertainty. The width of the 95% confidence intervals associated with predictions – 10 times for water and 100 times for trout – accurately represent the predictive certainty to be expected when models are applied in what is essentially a screening mode.

Because the model predictions were found to be highly uncertain, the results should be considered to be more qualitative than quantitative. In other words, comparative results from the model are expected to be reliable, but absolute numerical output is not. It would be inappropriate to base decision-making on a quantitative result from this model, without considering the magnitude of uncertainty associated with that result.

Further effort could be applied to evaluating model uncertainty. For PCBs, there are sufficient ambient data to perform a regionalized sensitivity analysis (Hornberger and Spear, 1981) on the model, which could better define reasonable probability distributions for model parameters. Parameter covariance, which was neglected, could also be considered in the uncertainty analysis. Some important model parameters, including particle transport parameters, are expected to be substantially cross-correlated. Neglecting this covariance inflates the uncertainty estimates. Parameter covariance may be estimated during model calibration. Application of these methods was, however, considered beyond the scope of this effort.

1.7 Dynamic Model Applications

The dynamic MICHTOX model was used to predict temporal changes in toxic chemical concentrations under transient conditions. The most important of these is the prediction of "lag time," the period of time for concentrations to respond to a change in loading. Dynamic simulations were also made for several PCBs management scenarios and for a hypothetical severe storm "event." Finally, uncertainty in the dynamic simulations will be examined, including consideration of factors not included in the model framework.

1.7.1 Toxic Chemical Lag Time

The most important dynamic prediction is lag time. It is the time required for a specific load reduction to achieve a desired water quality objective, such as attaining a water quality standard or lifting an advisory on fish consumption. The lag time depends upon the magnitude of the loading reduction, the difference between present and desired concentrations, and the intrinsic responsiveness of the system which is predicted by the model. Greater loading reductions will result in shorter lag times, although the difference may be small, and lag times will be longer to achieve lower concentration objectives.

The rate of concentration change (dc/dt) in response to a reduction in loading is determined by the magnitude of the load reduction as well as the model parameterization. Accordingly, dc/dt will be different for every load reduction, which severely limits the generality of model predictions. However, a relative concentration x may be defined:

$$x = \frac{c - c_f}{c_i - c_f}$$

where:

c_i = initial concentration before load reduction

c_f = final steady-state concentration at new load

for which the rate of change dx/dt is independent of the magnitude of load reduction, and is determined solely by the model parameterization for each toxic chemical. Thus, results from one dynamic simulation may be used to predict dx/dt for load reductions of any magnitude for each toxic chemical. Since dx/dt equals dc/dt if loading is completely eliminated, this "cutoff" simulation was used to determine rates of concentration change for each toxic chemical: a constant loading was eliminated after steady-state had been reached, and the subsequent decline in concentrations simulated for the next 30 years. Results of this simulation for each toxic chemical are presented in Table 1.16; the results for PCBs are also plotted in Figure 1.64. Simulated concentrations initially decline rapidly, particularly in water. Thereafter, the concentration decline approaches a steady, first-order loss rate in each media. Chemicals are ordered in the table according to this chemical loss rate for water and sediment, with HCB, PCBs, BaP, and heptachlor epoxide concentrations declining most rapidly.

Table 1.16. Predicted Long-Term Chemical Loss Rates for Lake Michigan Critical Pollutants Following Loading Reduction. First-Order Loss Rates in Units of 1/Year in Southern Lake Michigan

Chemical	Water	Sediment	Trout
HCB	0.16	0.16	0.16
PCBs	0.15	0.15	0.12
BaP	0.14	0.14	0.14
Heptachlor epoxide	0.12	0.13	0.12
Chlordane	0.091	0.093	0.092
DDT	0.085	0.086	0.086
Toxaphene	0.063	0.063	0.064
TCDF	0.063	0.063	0.063
TCDD	0.061	0.060	0.061
Lead	0.046	0.047	
Dieldrin	0.040	0.041	0.041

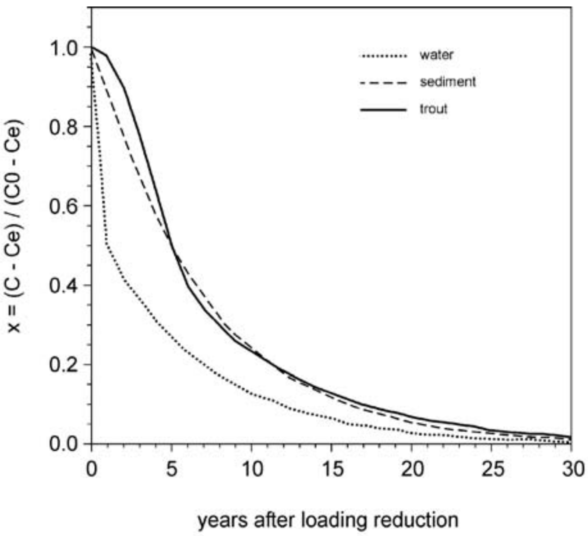


Figure 1.64. Predicted PCBs time response to loading reduction in southern Lake Michigan.

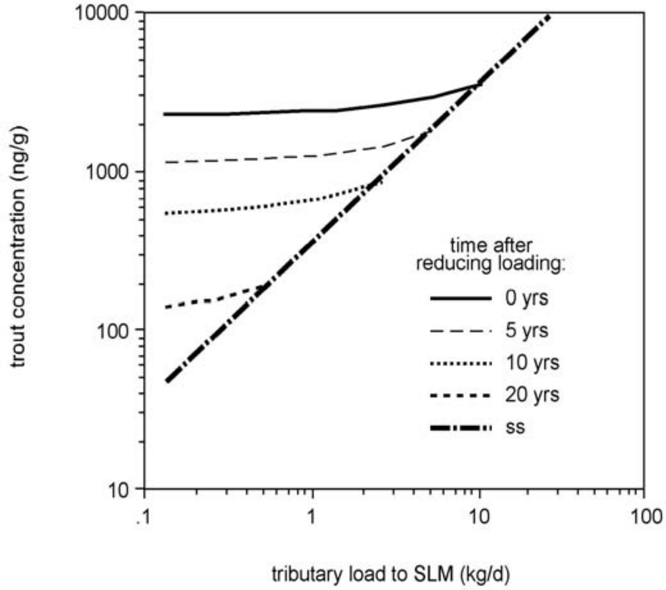


Figure 1.65. Response of trout PCBs concentrations at various times after reducing PCBs load (ss = steady-state).

The practical significance of lag time may be demonstrated in terms of the load-concentration relationship. At steady-state, concentrations are proportional to total loading. Thus the load-concentration relationship is linear: a 50% reduction in concentration is achieved by cutting the total chemical load in half. However, this outcome will only be achieved after a relatively long time. The maximum rate of concentration decline is controlled by the lake itself, and the effectiveness of loading reduction is constrained by this rate. This constraint causes the load-concentration relationship to diverge from linearity, as shown in Figure 1.65. For a given time after reducing total lake loading (0, 5, and 10 years), PCBs in trout will not decline below a limiting concentration, even if total load is reduced to zero. As time after reducing total load increases, the limiting trout concentration will decline, allowing smaller loads to become effective. Every five years, the limiting trout PCBs concentration decreases by about 50%. Only after a very long time will the load-concentration curves converge upon the steady-state relationship.

The loss rate predictions for concentrations in trout may be applied to tentatively evaluate available monitoring data for priority toxics in Lake Michigan. By comparing the load "cutoff" predictions to the trend in concentration data, the hypothesis that priority toxics loading has been essentially eliminated may be tested. If concentrations appear to decline as rapidly as the load "cutoff" predictions, then it may be concluded that the rate of decline is controlled by the long-term loss rates of the system. Figure 1.66 presents such a comparison for chlordane (data sources are indicated on figures). Although no clear trend of declining concentration is apparent in chlordane data, the slow rate of predicted concentration decline following load cutoff suggests that such a trend could be obscured by the variability of these data. Comparison of data to the load cutoff prediction for DDT is displayed in Figure 1.67. Because DDT concentrations are declining, at least as rapidly as the load cutoff prediction, DDT loading in recent years appears to be negligible. Essentially the same conclusion is drawn for dieldrin (Figure 1.68), PCBs (Figure 1.69), and TCDD (Figure 1.70). For TCDF, the comparison leads to an ambiguous result (Figure 1.71) particularly because the variability associated with this data is unknown. Generally, however, it appears that recent trends in trout concentration for these chemicals are consistent with model simulations of load "cutoff." It cannot be concluded from this that loads are zero; rather, it suggests that present loads are small in comparison to past loadings which have resulted in extensive sediment contamination. Further, this sediment reservoir maintains water column and biota chemical concentrations at their present levels. At

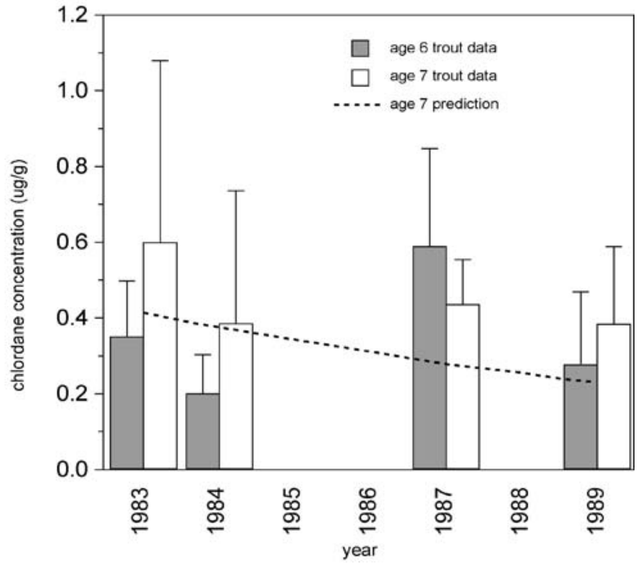


Figure 1.66. Simulation of chlordane in Lake Michigan trout (Michigan Department of Natural Resources, 1990).

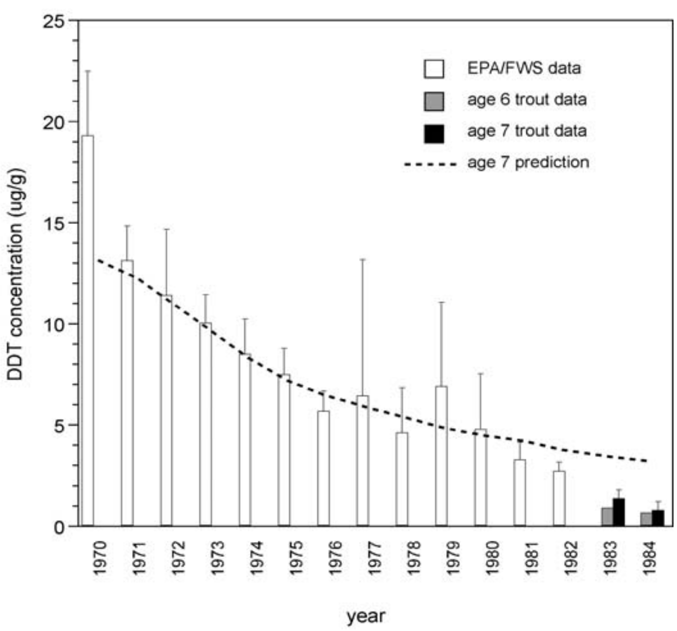


Figure 1.67. Simulation of DDT in Lake Michigan trout (DeVault *et al*., 1986; Michigan Department of Natural Resources, 1990).

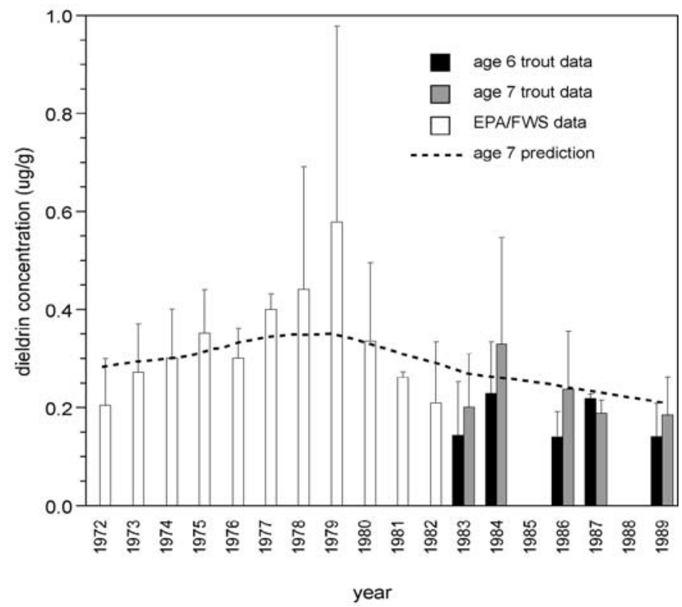


Figure 1.68. Simulation of dieldrin in Lake Michigan trout (DeVault *et al*., 1986; Michigan Department of Natural Resources, 1990).

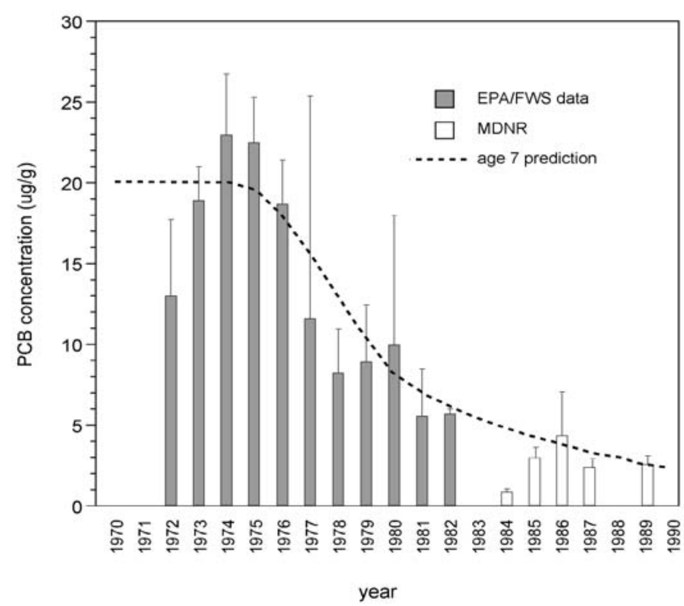


Figure 1.69. Load cutoff simulation of PCBs in Lake Michigan trout.

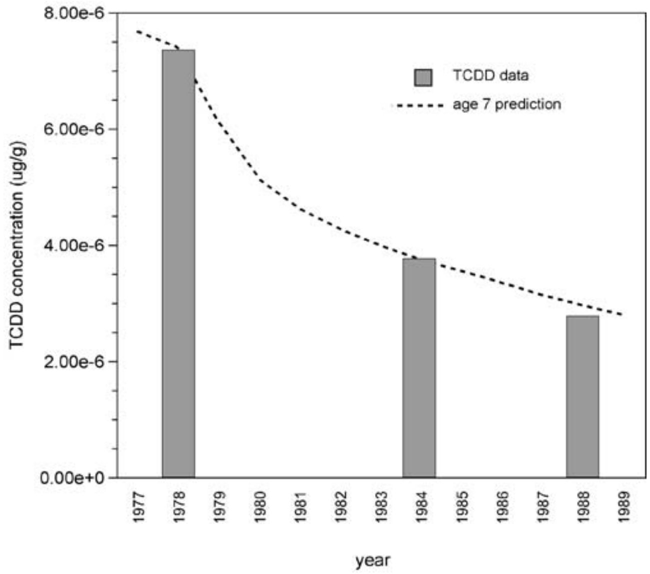


Figure 1.70. Tetrachlorodibenzo-p-dioxin simulation in Lake Michigan trout (U.S. Environmental Protection Agency, 1989b).

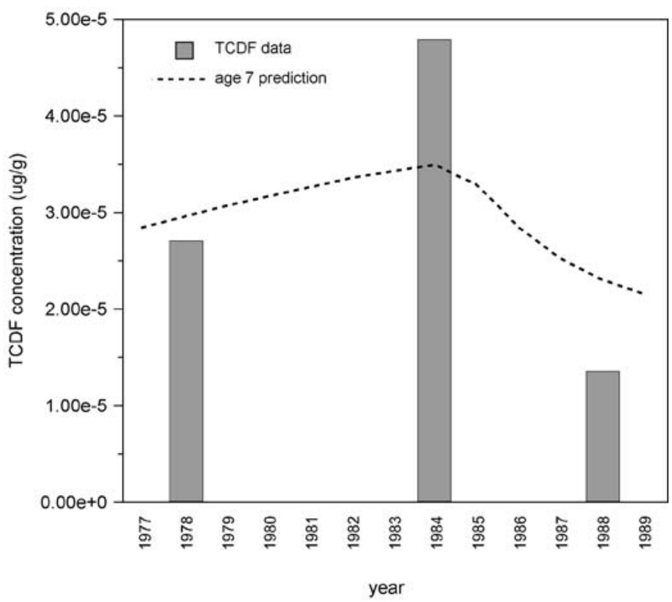


Figure 1.71. Tetrachlorodibenzofuran simulation in Lake Michigan trout (U.S. Environmental Protection Agency, 1989b).

some point in time, toxic chemical concentrations will likely re-equilibrate with loading, the condition defined/predicted by the steady-state model.

1.7.2 PCBs Fate and Transport Fluxes in Dynamic Simulations

Results of the dynamic model simulations provide estimates of the chemical mass fluxes in the lake, which indicate the magnitude of contaminant reservoirs and fate and transport pathways. For PCBs in 1989 (based upon the verification simulation), the mass in all model segments is 33,000 kg, 95% of which resides in the surficial sediment. This reservoir of in-place PCBs controls the residual concentrations predicted throughout the lake. Net volatilization of PCBs from the main lake is 1860 kg in 1989, while 530 kg volatilizes from Green Bay. The loss of PCBs with particle burial is 1200 kg; 95% of burial occurs in main lake sediments. In comparison, the transport (advection and dispersion) of PCBs from the lake through the Straits of Mackinac is only 16 kg. Transport from Green Bay to Lake Michigan is also very small: 3 kg. The prediction that net volatilization to the atmosphere is 150 times larger than the corresponding transport from either Green Bay or the whole lake should provide additional incentive to couple the mass balance for the water to that of the atmosphere. The predicted net volatilization fluxes are much larger than the estimated deposition fluxes to the lake, suggesting that chemicals volatilized from the lake may not be lost but instead transported and redeposited, possibly in the same lake or elsewhere in the Great Lakes basin.

1.7.3 Additional Dynamic Simulations for PCBs

Two additional applications of MICHTOX to the dynamic simulation of PCBs are presented. The first predicts the effectiveness of maximum theoretical controls of current PCBs loadings. The second simulates how an extreme storm event which disrupts the particle balance could impact current PCBs concentrations.

1.7.3.1 PCBs Control Scenarios

Polychlorinated biphenyls have been identified as a priority toxic in Lake Michigan because of persistent elevated concentrations in Lake Michigan biota, especially lake trout. Reduction of present atmospheric and tributary loadings may be contemplated by the LaMP as control actions to lower PCBs concentrations. Aside from issues of feasibility or expense, the effectiveness of PCBs load reduction upon reducing concentrations in lake trout should be considered before taking such action. To this end, MICHTOX was used to simulate the expected change in future southern Lake Michigan lake trout PCBs concentrations in response to load reduction scenarios initiated in 1990. A No-Action scenario was based upon extending the duration of the verification simulation and holding PCBs loadings constant after 1990. The second scenario was the elimination of tributary loading at 1990. The third scenario for controlling PCBs was to eliminate all loading (total), atmospheric as well as tributary. Resulting trout concentration predictions for the three scenarios are plotted in Figure 1.72. Trout PCBs concentrations are predicted to decline 55% in 10 years in the No-Action scenario. The additional reduction in predicted trout concentrations due to eliminating tributary PCBs loading is barely detectable, suggesting that controlling tributary loading alone will be ineffective for PCBs in southern Lake Michigan. The third, "Zero-Load" scenario is predicted to have a more substantial effect upon trout PCBs concentrations, resulting in a 74% reduction in 10 years. Viewed another way, these simulations suggest that a 2 µg/g (ppm) PCBs lake trout standard would be achieved five years sooner for the Zero-Load scenario than for No-Action. However, even for the Zero-Load scenario, 0.4 µg/g of PCBs would remain in trout after 20 years. According to these predictions, virtual elimination of external sources of PCBs will have, at best, only long-term effectiveness in reducing concentrations in Lake Michigan.

It should be noted that these predictions were extrapolated beyond the end of the verification simulation, which appeared to overpredict PCBs trout concentrations after 1980 by a factor of two. While this discrepancy was acceptable from the standpoint of preliminary verification, it leads to some ambiguity in predicting future PCBs concentrations. For

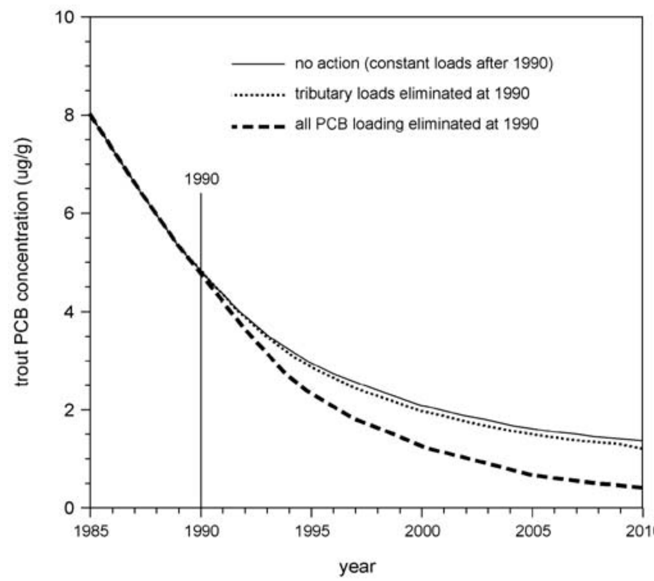


Figure 1.72. Predicted effectiveness of PCBs load reductions.

example, would the prediction be more accurate if the trout concentrations were lowered to match the data? This could be achieved by changing the loading time-series, the model calibration, or some combination of the two. Given the available information, this would be a somewhat arbitrary decision that would lead to different future predictions. It would be preferable to base predictions of future PCBs concentrations on a simulation which better matches present conditions. These conditions include sediment, trout, and water concentrations and atmospheric and non-atmospheric loads. The collection of data for the purpose of defining present conditions for PCBs or other priority toxics in Lake Michigan should be prioritized because this information will be essential for making reliable predictions of future toxic chemical concentrations.

1.7.3.2 Severe Storm Event

Analysis of chemical distribution in sediment cores indicates that normal sedimentation rates in the Great Lakes are periodically disrupted; these disruptions have been related chronologically to major storms (Robbins *et al*., 1978). Lick (1993) has suggested that such events are of considerable significance in determining the distribution, transport, and fate of particle - associated contaminants such as PCBs. To pursue this suggestion, the impact of such a severe storm on PCBs concentrations in Lake Michigan was simulated. A storm occurring in winter of 1990 was simulated; during the two-day event, the entire surficial sediment layer was eroded from the southern lake basin (Segment 11) and resuspended through the water column. Afterwards, particle fluxes were returned to their normal time-series values and the solids balance was allowed to recover. Predicted suspended particle and PCBs water concentrations in southern Lake Michigan are plotted in Figure 1.73.

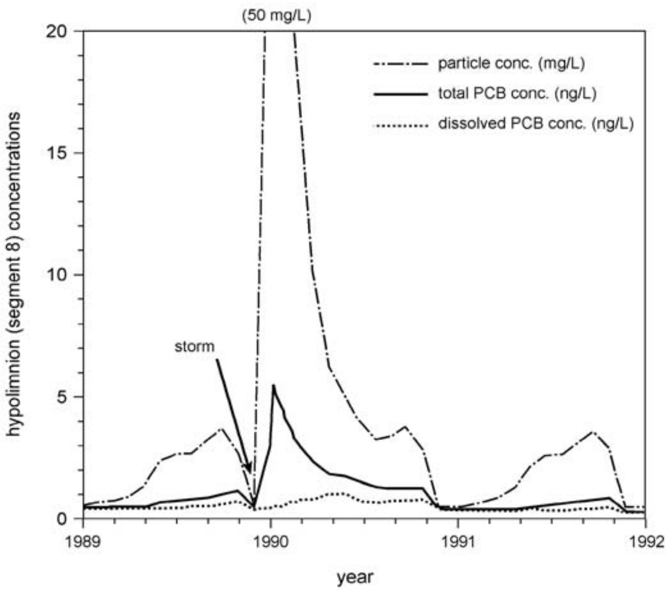


Figure 1.73. Simulation of storm event in southern Lake Michigan.

Maximum suspended particle concentrations of 50 mg/L were predicted throughout the water column immediately following the storm. Total water concentration jumps to over 5 ng/L, and elevated concentrations persist for about a year. The increase in dissolved concentration due to the storm is considerably less, however, due to the response of the partitioning model to increased particle concentrations. The dissolved fraction (f_d) of total PCBs decreases from 50-60% before the storm to only 9% during the event. In the surficial sediment (Figure 1.74), PCBs concentrations are depleted by the storm, with a small reduction in long-term concentrations. The PCBs concentration increase for trout (not plotted) is also relatively small. On an annual basis, the maximum increase in trout concentration, 4%, occurs the year following the storm with a diminishing effect in the following years.

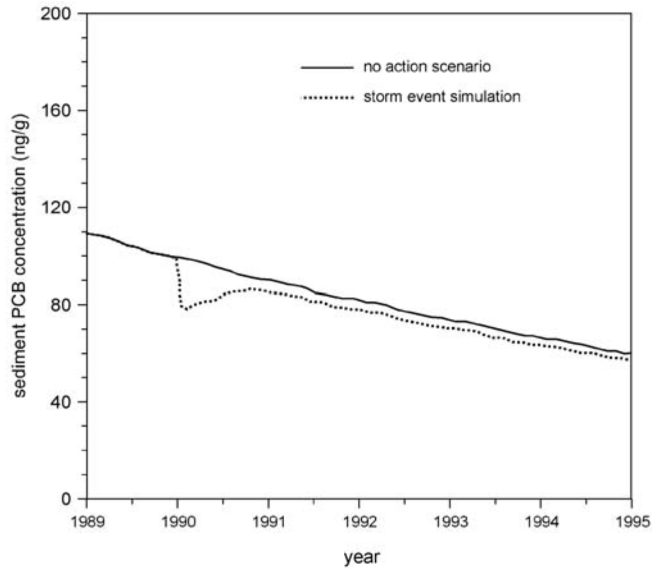


Figure 1.74. Effect of storm event on PCBs in southern Lake Michigan sediment.

Because most of the resuspended PCBs are partitioned into non-dissolved fractions, they are largely unavailable for accumulation by biota. Results of this simulation suggest that the effect of severe storms upon PCBs concentrations in the main lake are short-lived and do not lead to significant additional accumulation in biota.

1.7.4 Uncertainty in Dynamic Simulations

Dynamic model simulations are uncertain due to factors in addition to those considered in the steady-state model. These factors include the additional significant model parameter, the surficial sediment thickness, and uncertainty of initial conditions and the time-series of loadings. The surficial sediment thickness defines the residence time of particles and chemicals in the mixed layer, which controls the long-term rate of concentration change in the model. Sediment thickness was parameterized in MICHTOX according to values suggested by vertical concentration profiles of lead-210 and cesium-137 in sediment cores. In addition, this parameterization was verified for water column plutonium concentrations. However, the modeling assumption that the mixed-layer residence time will be the same for all toxic chemicals has not been validated. In particular, the thickness of the mixed layer may relate to the loading history of a particular chemical. If, for example, the loading of a chemical were to increase faster than the rate at which it could be incorporated and mixed throughout the surficial sediment layer, then the mixed layer thickness would effectively decrease. Intensity and depth of sediment mixing also depend upon the abundance and type of benthos; *Diporeia*, for instance, mix only the upper 1 to 2 cm of sediment (Eisenreich *et al*., 1989). A thinner surficial sediment thickness results in predictions of a more rapid change in concentrations. This sensitivity is demonstrated for the simulation of PCBs concentrations in trout in Figure 1.75. The "thin sediment" simulation, using a surficial sediment thickness of 1.1 cm (one-third the base parameterization), does predict PCBs concentration change in better agreement with the data. This simulation would also change the prediction of future PCBs concentrations, indicating less significant decline in concentrations over the next 10 years. The parameterization of surficial sediment thickness is, therefore, one potentially significant cause of uncertainty in dynamic model predictions.

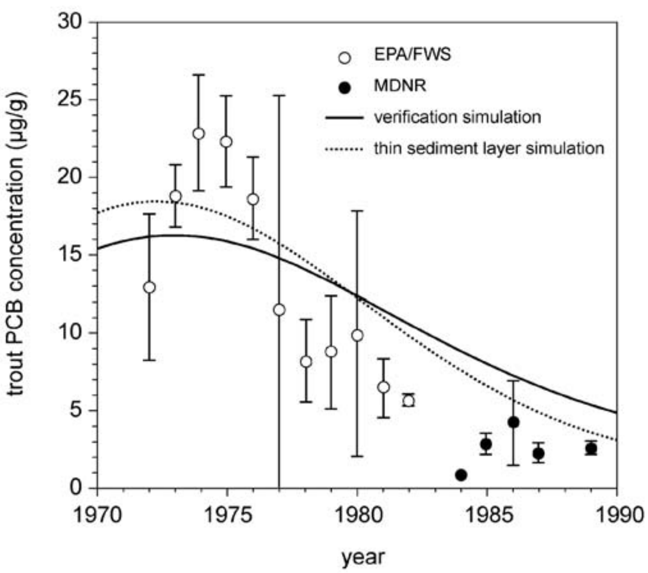


Figure 1.75. Sensitivity of PCBs concentrations in trout to thin (1.1 cm) surficial sediment layer thickness.

Another source of dynamic prediction uncertainty is the determination of initial concentration conditions for model simulations. If model simulations begin with a "clean" system, as was the case for MICHTOX verification, then this is not an issue. However, such simulations may result in excessively long model runs, and may not be possible for toxic chemicals whose past loadings are unknown. If, for instance, one wished to simulate trout PCBs concentrations after their maximum in 1974, the initial PCBs concentrations would have to be input. For age seven trout, this could range from 15 to 27 µg/g, according to the data. Depending upon the selection, quite different model predictions could result. However, even more critical is the selection of initial chemical concentrations in the surficial sediment, because under reduced loading conditions sediment concentrations "drive" the model simulation.

Computer resources were insufficient to perform full uncertainty analysis on the dynamic MICHTOX model. However, a limited test was run for PCBs to evaluate the significance of the factors discussed above, in relationship to those already considered for the steady-state model, upon uncertainty in dynamic simulations. Ten Monte Carlo simulations of the PCBs Zero-Load scenario were run; model parameters, including surficial sediment thickness, were varied by the Latin Hypercube method to simulate uncertainty. The results, for water and trout concentration predictions, are plotted in Figures 1.76 and 1.77. Although 10 runs are not sufficient to resolve the model output distributions, they do provide a qualitative indication of uncertainty in dynamic predictions. The lag time for a 90%

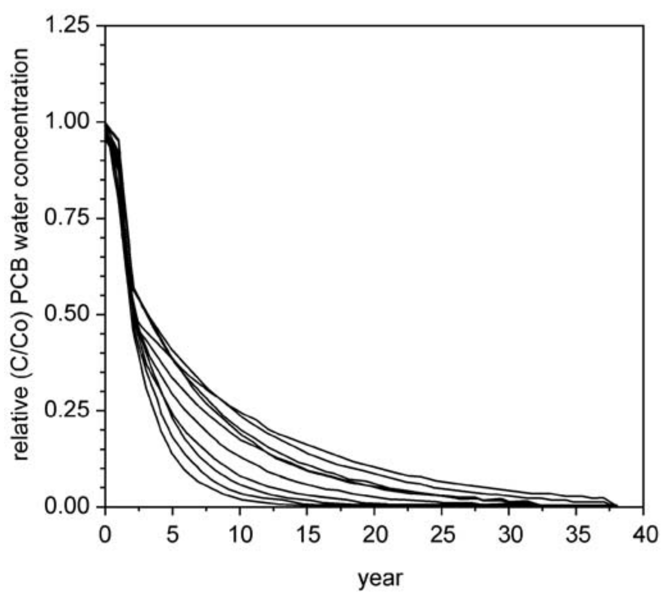


Figure 1.76. Predicted water PCBs concentrations for ten realizations of dynamic model.

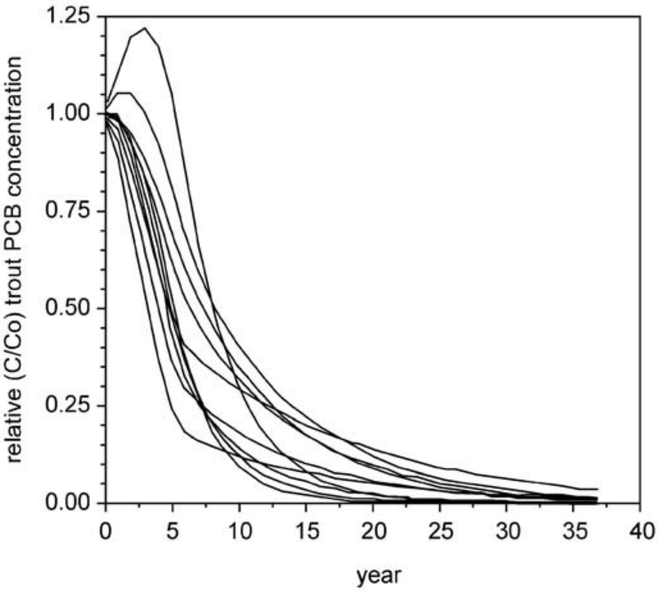


Figure 1.77. Predicted trout PCBs concentrations for ten realizations of dynamic model.

reduction in PCBs water concentration varied from six to 20 years, with a mean of 12 years. In trout, the 90% lag time varied from 10 to 24 years, with a mean of 16 years. The surficial sediment thickness was found to contribute more than 85% of the uncertainty in water concentration lag time predictions. For trout lag time predictions, the most significant source of uncertainty was the plankton BCF (30% of lag time variability). Twenty-four percent of the trout lag time variability could be attributed to the lag time in water concentrations. As was the case for the steady-state model, analysis reveals that the dynamic model predictions are highly uncertain. Consequently, as was the case for steady-state, quantitative results from the dynamic model simulations should not be considered reliable. Reducing this uncertainty would require additional calibration and/or verification data and measurement of critically uncertain parameters.

It should also be considered that the loading time-series are themselves somewhat speculative and uncertain. Historical loadings must usually be inferred from sedimentary records (plutonium being the notable exception) from which the loading time-series may not be fully deconvoluted (Christensen and Goetz, 1987). As a result, it may be difficult during calibration and verification to distinguish model error from errors in the loading time-series. This is demonstrated by comparing the verification and load cutoff simulations (Figures 1.31 and 1.69). If one compares the fit of these two simulations to the trout PCBs data, the cutoff of PCBs loads at 1974 would appear to be the better loading time-series. Because relatively little data are available to independently confirm the PCBs loading time-series developed for Lake Michigan, the loading history itself must be considered as a source of error to the simulation. Accurately determining loads is critical for detecting and correcting model errors and, ultimately, to reducing predictive uncertainty.

One additional aspect of MICHTOX which may lead to erroneous long-term predictions is the lack of structural variability in the bioaccumulation model. In particular, the MICHTOX trophic structure is static; the model neither predicts nor does it respond to factors such as changing forage composition, trophic status in response to nutrients, exotic species invasion, or fisheries management. Yet such factors do affect the trophic structure in the Great Lakes and may be expected to affect bioaccumulation at the top of the food chain. Long-term bioaccumulation simulations well-parameterized for present conditions are likely to diverge from future reality as the lake trophic structure varies. In some cases, the prediction divergence may be small, as was the predicted change in trout PCBs bioaccumulation due to benthic coupling. However, this may not generally be the case. Uncertainty in future bioaccumulation predictions due to the dynamics of trophic structure in the Great Lakes is, as far as existing bioaccumulation models are concerned, in the realm of unforeseeable possibilities.

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